

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## BEST AVAILABLE IMAGES

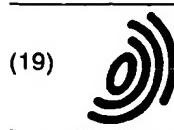
Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**



Europäisches Patentamt

European Patent Office

Office européen des brevets

(19)



(11)

EP 1 350 819 A1

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:

08.10.2003 Bulletin 2003/41

(51) Int Cl.7: C09D, 11/00, C09B 47/04,  
C09B 47/06, C09B 47/067

(21) Application number: 03007384.5

(22) Date of filing: 02.04.2003

(84) Designated Contracting States:  
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR  
HU IE IT LI LU MC NL PT RO SE SI SK TR  
Designated Extension States:  
AL LT LV MK

(30) Priority: 03.04.2002 JP 2002101347

(71) Applicant: FUJI PHOTO FILM CO., LTD.  
Kanagawa 250-01 (JP)

(72) Inventor: Ozawa, Takashi,  
Fuji Photo Film Co., Ltd.  
Shizuoka (JP)

(74) Representative: HOFFMANN - EITLE  
Patent- und Rechtsanwälte  
Arabellastrasse 4  
81925 München (DE)

### (54) Inkjet recording ink and inkjet recording method

(57) An ink comprising an aqueous medium and at least one dye represented by the formula (I) as defined herein, which is dissolved or dispersed in the aqueous medium, wherein the ink permeates into a recording medium having an image-receiving layer to a depth of 5 to 30 µm.

EP 1 350 819 A1

**Description****FIELD OF THE INVENTION**

5 [0001] The present invention relates to an inkjet recording ink which provides an image having high quality and excellent preservability and ensures excellent ejection stability.

**BACKGROUND OF THE INVENTION**

10 [0002] Accompanying recent overspreading of computers, inkjet printers are widely used for the printing on paper, film, cloth or the like not only in offices but also at homes.

[0003] The inkjet recording method includes a system of jetting out a liquid droplet by applying a pressure using a piezo element, a system of jetting out a liquid droplet by generating bubbles in an ink under heat, a system of using an ultrasonic wave, and a system of jetting out a liquid droplet by suction using an electrostatic force. The ink used for such inkjet recording systems includes an aqueous ink, an oily ink and a solid (fusion-type) ink. Among these inks, the aqueous ink is predominating in view of production, handleability, odor, safety and the like.

15 [0004] The dye used in such an inkjet recording ink is required to have high solubility in a solvent, enable high-density recording, provide good color, exhibit excellent fastness to light, heat, air, water and chemicals, ensure good fixing property to an image-receiving material and less blurring, give an ink having excellent storability, have high-purity and no toxicity, and be available at a low cost. However, it is very difficult to find out a dye satisfying these requirements in a high level. In particular, a dye having good cyan color and excellent weather resistance is strongly demanded.

20 [0005] Also, the inkjet recording is known to have a problem that a phenomenon of metal gloss called bronze which is deemed ascribable to regular reflected light on the surface of dye particle is sometimes observed and this deteriorates the image quality.

25

**SUMMARY OF THE INVENTION**

30 [0006] Accordingly, an object of the present invention is to provide an inkjet recording ink having good ejection stability, giving a high-quality image and ensuring good image preservability under severe conditions, which is an aqueous ink preferred in view of handleability, odor, safety and the like.

[0007] The above-described object can be attained by the followings. More specifically, according to the present invention, the following inkjet recording ink and inkjet recording method are provided.

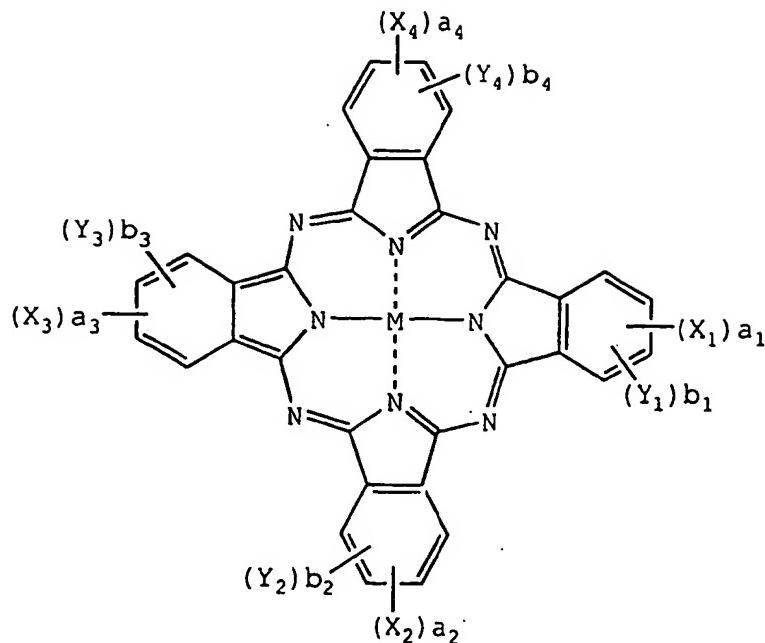
35 (1) An inkjet recording ink comprising an aqueous medium having dissolved or dispersed therein at least one dye represented by the following formula (I), wherein the ink permeates into a recording medium having an image-receiving layer to a depth of 5 to 30 µm:

40

45

50

55

**Formula (I) :**

wherein  $X_1$ ,  $X_2$ ,  $X_3$  and  $X_4$  each independently represents  $-SO_2-Z$ ,  $-SO_2-Z'$ ,  $-SO_2NR_1R_2$ , a sulfo group,  $-CONR_1R_2$  or  $-CO_2R_1$ , each  $Z$  independently represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic group,  $R_1$  and  $R_2$  each independently represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic group,  $Y_1$ ,  $Y_2$ ,  $Y_3$  and  $Y_4$  each independently represents a monovalent substituent,  $a_1$  to  $a_4$  and  $b_1$  to  $b_4$  each represents the number of substituent  $X_1$ ,  $X_2$ ,  $X_3$ ,  $X_4$ ,  $Y_1$ ,  $Y_2$ ,  $Y_3$  or  $Y_4$ ;  $a_1$  to  $a_4$  each independently represents a number of 0 to 4 but all are not 0 at the same time,  $b_1$  to  $b_4$  each independently represents a number of 0 to 3, provided that when at least one of  $a_1$  to  $a_4$  and  $b_1$  to  $b_4$  represents a number of 2 or more, corresponding plurality of substituents  $X_1$ ,  $X_2$ ,  $X_3$ ,  $X_4$ ,  $Y_1$ ,  $Y_2$ ,  $Y_3$  or  $Y_4$  may be the same or different, and  $M$  represents a hydrogen atom, a metal atom or an oxide, hydroxide or halide thereof.

(2) The ink as described in (1) above, wherein the dye represented by formula (I) is a dye represented by the following formula (II):

45

50

55

## Formula (II) :

5

10

15

20

25

30

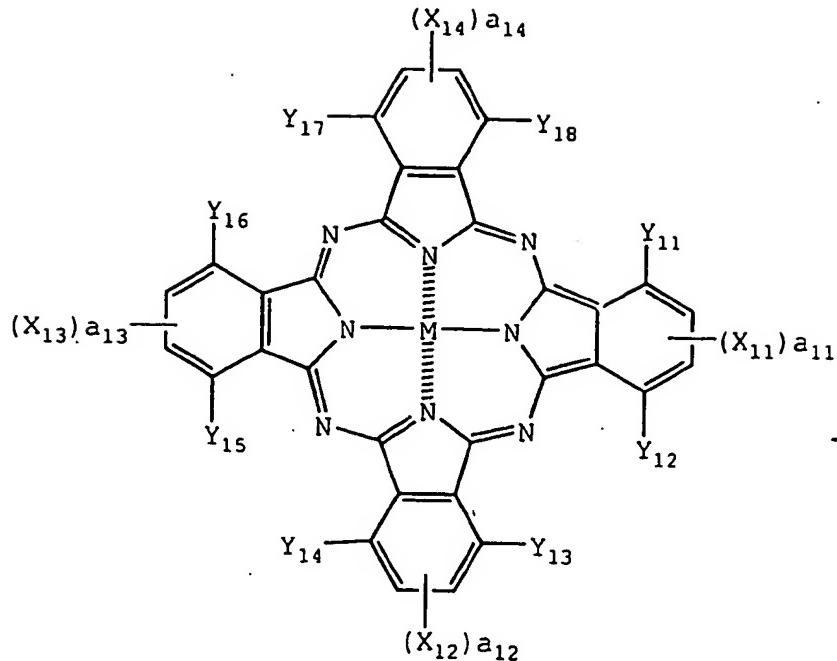
35

40

45

50

55



wherein  $X_{11}$  to  $X_{14}$ ,  $Y_{11}$  to  $Y_{18}$  and  $M$  have the same meanings as  $X_1$  to  $X_4$ ,  $Y_1$  to  $Y_4$  and  $M$  in formula (I), respectively, and  $a_{11}$  to  $a_{14}$  each independently represents an integer of 1 or 2.  
 (3) An inkjet recording method using the inkjet recording ink described in (1) or (2) above.  
 (4) An inkjet recording method comprising jetting out an ink droplet on an image-receiving material according to recording signals to record an image on the image-receiving material, the image-receiving material comprising a support having thereon an image-receiving layer containing a white inorganic pigment particle,

wherein the ink droplet comprises the inkjet recording ink described in (1) or (2) above.

#### DETAILED DESCRIPTION OF THE INVENTION

[0008] The present invention is described in detail below.

[0009] The dye used in the inkjet recording ink of the present invention is a phthalocyanine dye, preferably a dye represented by formula (I). The phthalocyanine dye is a dye having fastness but this dye is known to be inferior in the fastness to ozone gas when used as a dye for inkjet recording.

[0010] In the present invention, an electron withdrawing group is preferably introduced into the phthalocyanine skeleton to have an oxidation potential nobler than 1.0 V (vs SCE) and thereby reduce the reactivity with ozone which is an electrophilic agent. A nobler oxidation potential is more preferred and the oxidation potential is more preferably nobler than 1.1 V (vs SCE) and most preferably nobler than 1.2 V (vs SCE).

[0011] The oxidation potential value ( $E_{ox}$ ) can be easily measured by one skilled in the art and the method therefor is described, for example, in P. Delahay, New Instrumental Methods in Electrochemistry, Interscience Publishers (1954), A.J. Bard et al., Electrochemical Methods, John Wiley & Sons (1980), and Akira Fujishima et al., Denkikagaku Sokutei Ho (Electrochemical Measuring Method), Gihodo Shuppan Sha (1984).

[0012] More specifically, a test sample is dissolved to a concentration of  $1 \times 10^{-4}$  to  $1 \times 10^{-6}$  mol/liter in a solvent such as dimethylformamide or acetonitrile containing a supporting electrolyte such as sodium perchlorate or tetrapropylammonium perchlorate and the oxidation potential is measured as a value to SCE (saturated calomel electrode) using a cyclic voltammetry or a direct current polarography. This value sometimes deviates on the order of tens of millivolt due to the effect of liquid junction potential, liquid resistance of sample solution, or the like, however, the reproducibility of potential can be guaranteed by adding a standard sample (for example, hydroquinone).

- [0013] In order to univocally specify the potential, in the present invention, the value (vs SCE) measured by a direct current polarography in a dimethylformamide (concentration of dye: 0.001 mol dm<sup>-3</sup>) containing 0.1 mol dm<sup>-3</sup> of tetrapropylammonium perchlorate as the supporting electrolyte is used as the oxidation potential of the dye.
- [0014] The E<sub>ox</sub> value indicates the transferability of an electron from the sample to the electrode and as the value is larger (the oxidation potential is nobler), the electron is less transferable from the sample to the electrode, in other words, the oxidation less occurs. As for the relationship with the structure of compound, the oxidation potential becomes nobler by introducing an electron withdrawing group and becomes baser by introducing an electron donating group. In the present invention, the oxidation potential is preferably rendered nobler by introducing an electron withdrawing group into the phthalocyanine skeleton so as to reduce the reactivity with ozone which is an electrophilic agent. Accordingly, when the Hammett's substituent constant  $\sigma_p$  value as a measure for the electron withdrawing property or electron donating property of substituent is used, the oxidation potential can be rendered nobler by introducing a substituent having a large  $\sigma_p$  value, such as sulfinyl group, sulfonyl group and sulfamoyl group.
- [0015] For such potential control, the phthalocyanine dye represented by formula (I) is used in the present invention.
- [0016] In formula (I), X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub> and X<sub>4</sub> each independently represents -SO-Z, -SO<sub>2</sub>-Z, -SO<sub>2</sub>NR<sub>1</sub>R<sub>2</sub>, a sulfo group, -CONR<sub>1</sub>R<sub>2</sub> or -CO<sub>2</sub>R<sub>1</sub>. Among these substituents, preferred are -SO-Z, -SO<sub>2</sub>-Z, -SO<sub>2</sub>NR<sub>1</sub>R<sub>2</sub> and -CONR<sub>1</sub>R<sub>2</sub>, more preferred are -SO<sub>2</sub>-Z and -SO<sub>2</sub>NR<sub>1</sub>R<sub>2</sub>, and most preferred is -SO<sub>2</sub>-Z. In the case where at least one of a<sub>1</sub> to a<sub>4</sub> showing the number of substituent each represents a number of 2 or more, a corresponding plurality of substituents X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub> or X<sub>4</sub> may be the same or different and each independently represents any one of the above-described groups. X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub> and X<sub>4</sub> may be completely the same substituents, may be substituents of the same kind but partially different as in the case, for example, where X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub> and X<sub>4</sub> all are -SO<sub>2</sub>-Z and Zs are different from each other, or may include substituents different from each other, for example, -SO<sub>2</sub>-Z and -SO<sub>2</sub>NR<sub>1</sub>R<sub>2</sub>.
- [0017] Each Z independently represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group, preferably a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic group, and most preferably a substituted alkyl group, a substituted aryl group or a substituted heterocyclic group.
- [0018] R<sub>1</sub> and R<sub>2</sub> each independently represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group, preferably a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted heterocyclic group, most preferably a hydrogen atom, a substituted alkyl group, a substituted aryl group or a substituted heterocyclic group. However, it is not preferred that R<sub>1</sub> and R<sub>2</sub> both are a hydrogen atom.
- [0019] The substituted or unsubstituted alkyl group represented by R<sub>1</sub>, R<sub>2</sub> and Z is preferably an alkyl group having from 1 to 30 carbon atoms, more preferably a branched alkyl group because the solubility of dye and the stability of ink are improved, and still more preferably an alkyl group having an asymmetric carbon (use in the racemic form). Examples of the substituent include those described later as the substituent when Z, R<sub>1</sub>, R<sub>2</sub>, Y<sub>1</sub>, Y<sub>2</sub>, Y<sub>3</sub> and Y<sub>4</sub> can further have a substituent. In particular, a hydroxyl group, an ether group, an ester group, a cyano group, an amido group and a sulfonamido group are preferred because the aggregating property and fastness of dye are enhanced. Other than these, the alkyl group may be substituted by a halogen atom or an ionic hydrophilic group.
- [0020] The substituted or unsubstituted cycloalkyl group represented by R<sub>1</sub>, R<sub>2</sub> and Z is preferably a cycloalkyl group having from 5 to 30 carbon atoms, more preferably a cycloalkyl group having an asymmetric carbon (use in the racemic form) because the solubility of dye and the stability of ink are improved. Examples of the substituent include those described later as the substituent when Z, R<sub>1</sub>, R<sub>2</sub>, Y<sub>1</sub>, Y<sub>2</sub>, Y<sub>3</sub> and Y<sub>4</sub> can further have a substituent. In particular, a hydroxyl group, an ether group, an ester group, a cyano group, an amido group and a sulfonamido group are preferred because the aggregating property and fastness of dye are enhanced. Other than these, the cycloalkyl group may be substituted by a halogen atom or an ionic hydrophilic group.
- [0021] The substituted or unsubstituted alkenyl group represented by R<sub>1</sub>, R<sub>2</sub> and Z is preferably an alkenyl group having from 2 to 30 carbon atoms, more preferably a branched alkenyl group because the solubility of dye and the stability of ink are improved, and still more preferably an alkenyl group having an asymmetric carbon (use in the racemic form). Examples of the substituent include those described later as the substituent when Z, R<sub>1</sub>, R<sub>2</sub>, Y<sub>1</sub>, Y<sub>2</sub>, Y<sub>3</sub> and Y<sub>4</sub> can further have a substituent. In particular, a hydroxyl group, an ether group, an ester group, a cyano group, an amido group and a sulfonamido group are preferred because the aggregating property and fastness of dye are enhanced. Other than these, the alkenyl group may be substituted by a halogen atom or an ionic hydrophilic group.
- [0022] The substituted or unsubstituted aralkyl group represented by R<sub>1</sub>, R<sub>2</sub> and Z is preferably an aralkyl group having from 7 to 30 carbon atoms, more preferably a branched aralkyl group because the solubility of dye and the stability of ink are improved, and still more preferably an aralkyl group having an asymmetric carbon (use in the racemic form). Examples of the substituent include those described later as the substituent when Z, R<sub>1</sub>, R<sub>2</sub>, Y<sub>1</sub>, Y<sub>2</sub>, Y<sub>3</sub> and Y<sub>4</sub> can further have a substituent. In particular, a hydroxyl group, an ether group, an ester group, a cyano group, an amido

group and a sulfonamido group are preferred because the aggregating property and fastness of dye are enhanced. Other than these, the aralkyl group may be substituted by a halogen atom or an ionic hydrophilic group. Incidentally, the number of carbon atoms in the alkyl group does not contain carbon atoms of substituents and this applies to other groups.

- 5 [0023] The substituted or unsubstituted aryl group represented by R<sub>1</sub>, R<sub>2</sub> and Z is preferably an aryl group having from 6 to 30 carbon atoms. Examples of the substituent include those described later as the substituent when Z, R<sub>1</sub>, R<sub>2</sub>, Y<sub>1</sub>, Y<sub>2</sub>, Y<sub>3</sub> and Y<sub>4</sub> can further have a substituent. In particular, an electron withdrawing group is preferred because the dye can be noble in the oxidation potential and improved in the fastness.
- 10 [0024] Examples of the electron withdrawing group for use in the present invention include those having a positive Hammett's substituent constant  $\sigma_p$  value. Among these, preferred are a halogen atom, a heterocyclic group, a cyano group, a carboxyl group, an acylamino group, a sulfonamido group, a sulfamoyl group, a carbamoyl group, a sulfonyl group, an imido group, an acyl group, a sulfo group and a quaternary ammonium group, more preferred are a cyano group, a carboxyl group, a sulfamoyl group, a carbamoyl group, a sulfonyl group, an imido group, an acyl group, a sulfo group and a quaternary ammonium group.
- 15 [0025] The heterocyclic group represented by R<sub>1</sub>, R<sub>2</sub> and Z is preferably a 5- or 6-membered ring and the ring may be further condensed. Also, the heterocyclic group may be an aromatic heterocyclic group or a non-aromatic heterocyclic group. Examples of the heterocyclic group represented by R<sub>1</sub>, R<sub>2</sub> and Z are shown below in the form of a heterocyclic ring by omitting the substitution site. The substitution site is not limited and for example, pyridine may be substituted at the 2-position, 3-position and 4-position. Examples include pyridine, pyrazine, pyrimidine, pyridazine, triazine, quinoline, isoquinoline, quinazoline, cinnoline, phthalazine, quinoxaline, pyrrole, indole, furan, benzofuran, thiophene, benzo thiophene, pyrazole, imidazole, benzimidazole, triazole, oxazole, benzoxazole, thiazole, benzothiazole, isothiazole, benzisothiazole, thiadiazole, isoxazole, benzisoxazole, pyrrolidine, piperidine, piperazine, imidazolidine and thiazoline. In particular, an aromatic heterocyclic group is preferred. Preferred examples thereof include, shown in the same manner as above, pyridine, pyrazine, pyrimidine, pyridazine, triazine, pyrazole, imidazole, benzimidazole, triazole, thiazole, benzothiazole, isothiazole, benzisothiazole and thiadiazole. These groups each may have a substituent and examples of the substituent include those described later as the substituent when Z, R<sub>1</sub>, R<sub>2</sub>, Y<sub>1</sub>, Y<sub>2</sub>, Y<sub>3</sub> and Y<sub>4</sub> can further have a substituent. Preferred substituents are the same as the above-described substituents of the aryl group and more preferred substituents are the same as the above-described more preferred substituents of the aryl group.
- 20 [0026] Y<sub>1</sub>, Y<sub>2</sub>, Y<sub>3</sub> and Y<sub>4</sub> each independently represents a hydrogen atom, a halogen atom, an alkyl group, a cycloalkyl group, an alkenyl group, an aralkyl group, an aryl group, a heterocyclic group, a cyano group, a hydroxyl group, a nitro group, an amino group, an alkylamino group, an alkoxy group, an aryloxy group, an acylamino group, an arylamino group, a ureido group, a sulfamoylamino group, an alkylthio group, an arylthio group, an alkoxy carbonylamino group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, an alkoxy carbonyl group, a heterocyclic oxy group, an azo group, an acyloxy group, a carbamoyloxy group, a silyloxy group, an aryloxycarbonyl group, an aryloxycarbonylamino group, an imido group, a heterocyclic thio group, a phosphoryl group, an acyl group, a carboxyl group or a sulfo group. These substituents each may further have a substituent.
- 25 [0027] Among these, preferred are a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a cyano group, an alkoxy group, an amido group, a ureido group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, an alkoxy carbonyl group, a carboxyl group and a sulfo group, more preferred are a hydrogen atom, a halogen atom, a cyano group, a carboxyl group and a sulfo group, and most preferred is a hydrogen atom.
- 30 [0028] When Z, R<sub>1</sub>, R<sub>2</sub>, Y<sub>1</sub>, Y<sub>2</sub>, Y<sub>3</sub> and Y<sub>4</sub> each is a group which can further have a substituent, the group may further have the following substituent.
- 35 [0029] Examples of the substituent include a linear or branched alkyl group having from 1 to 12 carbon atoms, a linear or branched aralkyl group having from 7 to 18 carbon atoms, a linear or branched alkenyl group having from 2 to 12 carbon atoms, a linear or branched alkynyl group having from 2 to 12 carbon atoms, a linear or branched cycloalkyl group having from 3 to 12 carbon atoms, a linear or branched cycloalkenyl group having from 3 to 12 carbon atoms (these groups each is preferably a group having a branched chain because the solubility of dye and the stability of ink are improved, more preferably a group having an asymmetric carbon, e.g., methyl, ethyl, propyl, isopropyl, sec-butyl, tert-butyl, 2-ethylhexyl, 2-methylsulfonylethyl, 3-phenoxypropyl, trifluoromethyl, cyclopentyl), a halogen atom (e.g., chlorine, bromine), an aryl group (e.g., phenyl, 4-tert-butylphenyl, 2,4-di-tert-arylphenyl), a heterocyclic group (e.g., imidazolyl, pyrazolyl, triazolyl, 2-furyl, 2-thienyl, 2-pyrimidinyl, 2-benzothiazolyl), a cyano group, a hydroxyl group, a nitro group, a carboxy group, an amino group, an alkyloxy group (e.g., methoxy, ethoxy, 2-methoxyethoxy, 2-methanesulfonyloxy), an aryloxy group (e.g., phenoxy, 2-methylphenoxy, 4-tert-butylphenoxy, 3-nitrophenoxy, 3-tert-butyloxycarbamoylphenoxy, 3-methoxycarbamoyl), an acylamino group (e.g., acetamido, benzamido, 4-(3-tert-butyl-4-hydroxyphenoxy)butanamido), an alkylamino group (e.g., methylamino, butylamino, diethylamino, methylbutylamino), an anilino group (e.g., phenylamino, 2-chloroanilino), a ureido group (e.g., phenylureido, methylureido, N,N-dibutylureido), a sulfamoylamino group (e.g., N,N-dipropylsulfamoylamino), an alkylthio group (e.g., methylthio, octylthio, 2-phenox-

5     yethylthio), an arylthio group (e.g., phenylthio, 2-butoxy-5-tert-octylphenylthio, 2-carboxyphenylthio), an alkyloxycarbonylamino group (e.g., methoxycarbonylamino), a sulfonamido group (e.g., methanesulfonamido, benzenesulfonamido, p-toluenesulfonamido), a carbamoyl group (e.g., N-ethylcarbamoyl, N,N-dibutylcarbamoyl), a sulfamoyl group (e.g., N-ethylsulfamoyl, N,N-dipropylsulfamoyl, N-phenylsulfamoyl), a sulfonyl group (e.g., methanesulfonyl, octanesulfonyl, benzenesulfonyl, toluenesulfonyl), an alkyloxycarbonyl group (e.g., methoxycarbonyl, butyloxycarbonyl), a heterocyclic oxy group (e.g., 1-phenyltetrazol-5-oxy, 2-tetrahydro-pyranloxy), an azo group (e.g., phenylazo, 4-methoxyphenylazo, 4-pivaloylaminophenylazo, 2-hydroxy-4-propanoylphenylazo), an acyloxy group (e.g., acetoxy), a carbamoyloxy group (e.g., N-methylcarbamoyloxy, N-phenyl-carbamoyloxy), a silyloxy group (e.g., trimethylsilyloxy, dibutylmethylsilyloxy), an aryloxycarbonylamino group (e.g., phenoxy carbonylamino), an imido group (e.g., N-succinimido, N-phthalimido), a heterocyclic thio group (e.g., 2-benzothiazolylthio, 2,4-di-phenoxy-1,3,5-triazole-6-thio, 2-pyridylthio), a sulfinyl group (e.g., 3-phenoxypropylsulfinyl), a phosphonyl group (e.g., phenoxyphosphonyl, octyloxyphosphonyl, phenylphosphonyl), an aryloxycarbonyl group (e.g., phenoxy carbonyl), an acyl group (e.g., acetyl, 3-phenylpropanoyl, benzoyl), and an ionic hydrophilic group (e.g., carboxyl, sulfo, phosphono, quaternary ammonium).

10    [0030] In the case where the phthalocyanine dye represented by formula (I) is water-soluble, the dye preferably has an ionic hydrophilic group. Examples of the ionic hydrophilic group include a sulfo group, a carboxyl group, a phosphono group and a quaternary ammonium group. Among these ionic hydrophilic groups, preferred are a carboxyl group, a phosphono group and a sulfo group, more preferred are a carboxyl group and a sulfo group. The carboxyl group, the phosphono group and the sulfo group each may be in the form of a salt and examples of the counter ion for forming the salt include ammonium ion, alkali metal ion (e.g., lithium ion, sodium ion, potassium ion) and organic cation (e.g., tetramethylammonium ion, tetramethylguanidium ion, tetramethylphosphonium). Among these counter ions, an alkali metal salt is preferred and a lithium salt is more preferred because this salt enhances the solubility of dye and improves the stability of ink.

15    [0031] As for the number of ionic hydrophilic groups, the phthalocyanine dye preferably has at least two ionic hydrophilic groups, more preferably at least two sulfo groups and/or carboxyl groups, within one molecule.

20    [0032] a<sub>1</sub> to a<sub>4</sub> and b<sub>1</sub> to b<sub>4</sub> each represents the number of substituent X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub>, X<sub>4</sub>, Y<sub>1</sub>, Y<sub>2</sub>, Y<sub>3</sub> or Y<sub>4</sub>. a<sub>1</sub> to a<sub>4</sub> each independently represents a number of 0 to 4 but all are not 0 at the same time. b<sub>1</sub> to b<sub>4</sub> each independently represents a number of 0 to 4. When at least one of a<sub>1</sub> to a<sub>4</sub> and b<sub>1</sub> to b<sub>4</sub> each represents a number of 2 or more, a corresponding plurality of substituents of at least one of X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub>, X<sub>4</sub>, Y<sub>1</sub>, Y<sub>2</sub>, Y<sub>3</sub> or Y<sub>4</sub> may be the same or different.

25    [0033] a<sub>1</sub> and b<sub>1</sub> each independently represents a number of 0 to 4 satisfying the relationship of a<sub>1</sub>+b<sub>1</sub>=4. In particular, a combination that a<sub>1</sub> represents 1 or 2 and b<sub>1</sub> represents 3 or 2 is preferred, and a combination that a<sub>1</sub> represents 1 and b<sub>1</sub> represents 3 is most preferred.

30    [0034] The same relationship as that between a<sub>1</sub> and b<sub>1</sub> is present in each of the pairs a<sub>2</sub> and b<sub>2</sub>, a<sub>3</sub> and b<sub>3</sub>, and a<sub>4</sub> and b<sub>4</sub>, and the preferred combination is also the same.

35    [0035] M represents a hydrogen atom, a metal element or an oxide, hydroxide or halide thereof.

40    [0036] M is preferably a hydrogen atom, a metal element such as Li, Na, K, Mg, Ti, Zr, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, Cu, Ag, Au, Zn, Cd, Hg, Al, Ga, In, Si, Ge, Sn, Pb, Sb and Bi, an oxide such as VO and GeO, a hydroxide such as Si(OH)<sub>2</sub>, Cr(OH)<sub>2</sub> and Sn(OH)<sub>2</sub>, or a halide such as AlCl, SiCl<sub>2</sub>, VCl, VCl<sub>2</sub>, VOCl, FeCl, GaCl and ZrCl.

45    [0037] Among these, preferred are Cu, Ni, Zn and Al, and most preferred is Cu.

50    [0038] Also, Pc (phthalocyanine ring) may form a dimer (for example, Pc-M-L-M-Pc) or a trimer through L (divalent linking group). At this time, Ms may be the same or different.

55    [0039] The divalent linking group represented by L is preferably an oxy group -O-, a thio group -S-, a carbonyl group -CO-, a sulfonyl group -SO<sub>2</sub>-, an imino group -NH-, a methylene group -CH<sub>2</sub>- or a group formed by combining two or more of these groups.

60    [0040] As for the preferred combination of substituents in the compound represented by formula (I), a compound where at least one of various substituents is the preferred group is preferred, a compound where a larger number of various substituents are the preferred groups is more preferred, and a compound where all substituents are the preferred groups is most preferred.

65    [0041] Among the phthalocyanine dyes represented by formula (I), a phthalocyanine dye having a structure represented by formula (II) is preferred. The phthalocyanine dye represented by formula (II) of the present invention is described in detail below.

70    [0042] In formula (II), X<sub>11</sub> to X<sub>14</sub> and Y<sub>11</sub> to Y<sub>18</sub> have the same meanings as X<sub>1</sub> to X<sub>4</sub> and Y<sub>1</sub> to Y<sub>4</sub> in formula (I), respectively, and preferred examples are also the same. M has the same meaning as M in formula (I) and preferred examples are also the same.

75    [0043] In formula (II), a<sub>11</sub> to a<sub>14</sub> each independently represents an integer of 1 or 2 and preferably satisfy 4≤a<sub>11</sub>+a<sub>12</sub>+a<sub>13</sub>+a<sub>14</sub>≤6, and a<sub>11</sub>=a<sub>12</sub>=a<sub>13</sub>=a<sub>14</sub>=1 is more preferred.

80    [0044] X<sub>11</sub>, X<sub>12</sub>, X<sub>13</sub> and X<sub>14</sub> may be completely the same substituents, may be substituents of the same kind but partially different as in the case, for example, where X<sub>11</sub>, X<sub>12</sub>, X<sub>13</sub> and X<sub>14</sub> all are -SO<sub>2</sub>-Z and Zs are different from each

other, or may include substituents different from each other, for example, -SO<sub>2</sub>-Z and -SO<sub>2</sub>NR<sub>1</sub>R<sub>2</sub>.

[0045] In the phthalocyanine dye represented by formula (II), the following combination of substituents is particularly preferred.

[0046] X<sub>11</sub> to X<sub>14</sub> each independently represents preferably -SO-Z, -SO<sub>2</sub>-Z, -SO<sub>2</sub>NR<sub>1</sub>R<sub>2</sub> or -CONR<sub>1</sub>R<sub>2</sub>, more preferably -SO<sub>2</sub>Z or -SO<sub>2</sub>NR<sub>1</sub>R<sub>2</sub>, most preferably -SO<sub>2</sub>-Z.

[0047] Each Z independently represents preferably a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic group, and most preferably a substituted alkyl group, a substituted aryl group or a substituted heterocyclic group. In particular, the case where an asymmetric carbon is present in the substituent (use in the racemic form) is preferred because the solubility of dye and the stability of ink are enhanced. Also, the case where a hydroxyl group, an ether group, an ester group, a cyano group, an amido group or a sulfonamido group is present in the substituent is preferred because the aggregating property and fastness are improved.

[0048] R<sub>1</sub> and R<sub>2</sub> each independently represents preferably a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic group, and most preferably a hydrogen atom, a substituted alkyl group, a substituted aryl group or a substituted heterocyclic group. However, it is not preferred that R<sub>1</sub> and R<sub>2</sub> both are a hydrogen atom. In particular, the case where an asymmetric carbon is present in the substituent (use in the racemic form) is preferred because the solubility of dye and the stability of ink are enhanced. Also, the case where a hydroxyl group, an ether group, an ester group, a cyano group, an amido group or a sulfonamido group is present in the substituent is preferred because the aggregating property and fastness are improved.

[0049] Y<sub>11</sub> to Y<sub>18</sub> each independently represents preferably a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a cyano group, an alkoxy group, an amido group, a ureido group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, an alkoxy carbonyl group, a carboxyl group or a sulfo group, more preferably a hydrogen atom, a halogen atom, a cyano group, a carboxyl group or a sulfo group, and most preferably a hydrogen atom.

[0050] a<sub>11</sub> to a<sub>14</sub> each independently represents preferably 1 or 2 and it is particularly preferred that all are 1.

[0051] M represents a hydrogen atom, a metal element or an oxide, hydroxide or halide thereof, more preferably Cu, Ni, Zn or Al, and most preferably Cu.

[0052] In the case where the phthalocyanine dye represented by formula (II) is water-soluble, the dye preferably has an ionic hydrophilic group. Examples of the ionic hydrophilic group include a sulfo group, a carboxyl group, a phosphono group and a quaternary ammonium group. Among these ionic hydrophilic groups, preferred are a carboxyl group, a phosphono group and a sulfo group, more preferred are a carboxyl group and a sulfo group. The carboxyl group, the phosphono group and the sulfo group each may be in the form of a salt and examples of the counter ion for forming the salt include ammonium ion, alkali metal ion (e.g., lithium ion, sodium ion, potassium ion) and organic cation (e.g., tetramethylammonium ion, tetramethylguanidium ion, tetramethylphosphonium). Among these counter ions, an alkali metal salt is preferred and a lithium salt is more preferred because this salt enhances the solubility of dye and improves the stability of ink.

[0053] As for the number of ionic hydrophilic groups, the phthalocyanine dye preferably has at least two ionic hydrophilic groups, more preferably at least two sulfo groups and/or carboxyl groups, within one molecule.

[0054] As for the preferred combination of substituents in the compound represented by formula (II), a compound where at least one of various substituents is the preferred group is preferred, a compound where a larger number of various substituents are the preferred groups is more preferred, and a compound where all substituents are the preferred groups is most preferred.

[0055] As for the chemical structure of the phthalocyanine dye of the present invention, at least one electron withdrawing group such as sulfinyl group, sulfonyl group and sulfamoyl group is preferably introduced into respective four benzene rings of phthalocyanine such that the total of *op* values of the substituents in the entire phthalocyanine skeleton becomes 1.6 or more.

[0056] The Hammett's substituent constant *op* value is briefly described. The Hammett's rule is a rule of thumb advocated by L.P. Hammett in 1935 so as to quantitatively discuss the effect of substituent on the reaction or equilibrium of benzene derivatives and its propriety is widely admitted at present. The substituent constant determined by the Hammett's rule includes a *op* value and a *om* value and these values can be found in a large number of general publications but these are described in detail, for example, in J.A. Dean (compiler), Lange's Handbook of Chemistry, 12th ed., McGraw-Hill (1979), and Kagakuno Ryoiki (Chemistry Region), special number, No. 122, pp. 96-103, Nankodo (1979).

[0057] Generally, in view of the synthesis method, the phthalocyanine derivative represented by formula (I) is inevitably a mixture of analogues differing in the site where the substituents X<sub>n</sub> (n=1 to 4) and Y<sub>m</sub> (m=1 to 4) are introduced and in the number of the substituents introduced. Accordingly, these analogue mixtures are statistically averaged and represented by a formula in many cases. In the present invention, it has been found that when these analogue mixtures are classified into the following three types, a specific mixture is particularly preferred. The phthalocyanine-base dye

analogue mixtures represented by formulae (I) and (II) are defined by classifying these into the following three types based on the substitution site.

5 (1)  $\beta$ -Position substitution type:

[0058] A phthalocyanine dye having specific substituents at the 2- and/or 3-position, the 6- and/or 7-position, the 10- and/or 11-position, and the 14- and/or 15-position.

10 (2)  $\alpha$ -Position substitution type:

[0059] A phthalocyanine dye having specific substituents at the 1- and/or 4-position, the 5- and/or 8-position, the 9-and/or 12-position, and the 13- and/or 16-position.

15 (3)  $\alpha,\beta$ -Position mixed substitution type:

[0060] A phthalocyanine dye having specific substitutions at the 1- to 16-positions without any regularity.

[0061] In the present invention, phthalocyanine dye derivatives different in the structure (particularly in the substitution site) are described by using these  $\beta$ -position substitution type,  $\alpha$ -position substitution type and  $\alpha,\beta$ -position mixed substitution type.

20 [0062] The phthalocyanine derivative for use in the present invention can be synthesized by combining the methods described or cited, for example, in Shirai and Kobayashi, Phthalocyanine -Kagaku to Kino- (Phthalocyanine -Chemistry and Function-), pp. 1-62, IPC, and C.C. Leznoff and A.B.P. Lever, Phthalocyanines - Properties and Applications, pp. 1-54, VCH, or methods analogous thereto.

25 [0063] The phthalocyanine compound represented by formula (I) of the present invention can be synthesized, for example, through sulfonation, sulfonyl chloridation and amidation of an unsubstituted phthalocyanine compound as described in International Patents 00/17275, 00/08103, 00/08101 and 98/41853 and JP-A-10-36471 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"). In this case, sulfonation may take place at any site of the phthalocyanine nucleus and the number of sites sulfonated is difficult to control. Accordingly, when a sulfo group is introduced under such reaction conditions, the site and number of sulfo groups introduced into the product cannot be specified and a mixture of those different in the number of substituents or in the substitution site inevitably results. If the compound of the present invention is synthesized starting from such a product, the compound of the present invention is obtained as an  $\alpha,\beta$ -position mixed substitution type mixture containing several kinds of compounds different in the number of substituents or in the substitution site because the number of sulfamoyl groups substituted on the heterocyclic ring or their substitution sites cannot be specified.

30 [0064] As described above, for example, when many electron withdrawing groups such as sulfamoyl group are introduced into the phthalocyanine nucleus, the oxidation potential becomes nobler and the ozone resistance is increased. However, according to the above-described synthesis method, a phthalocyanine dye where the number of electron withdrawing groups introduced is small, namely, the oxidation potential is baser, is inevitably mingled. Accordingly, in order to improve the ozone resistance, it is preferred to use a synthesis method where the production of a compound having a baser oxidation potential is suppressed.

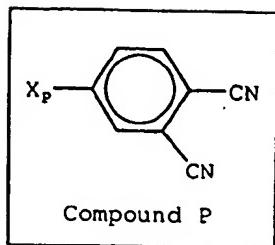
35 [0065] On the other hand, the phthalocyanine compound represented by formula (II) of the present invention can be synthesized, for example, by reacting a phthalonitrile derivative (Compound P) shown below and/or a diiminoisoindoline derivative (Compound Q) shown below with a metal derivative represented by formula (III) or may be derived from a tetrasulfophthalocyanine compound obtained by reacting a 4-sulfophthalonitrile derivative (Compound R) shown below with a metal derivative represented by formula (III).

50

55

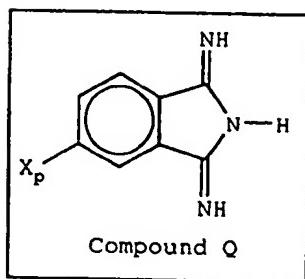
5

10



15

20



30

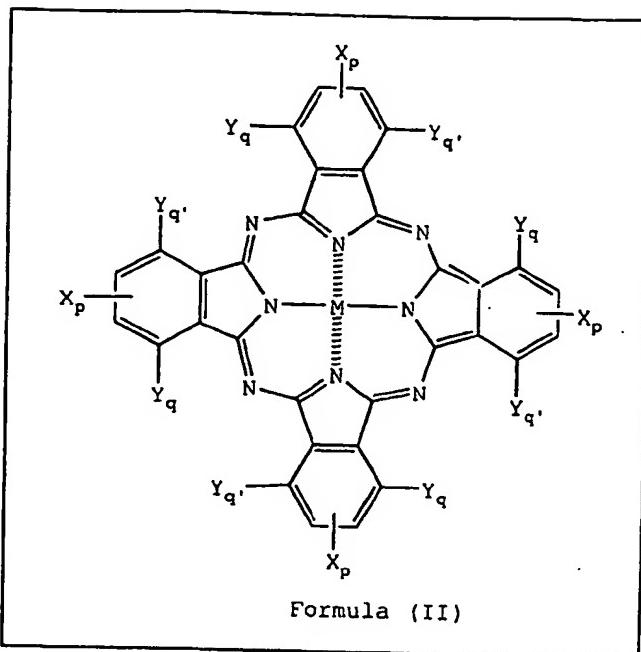
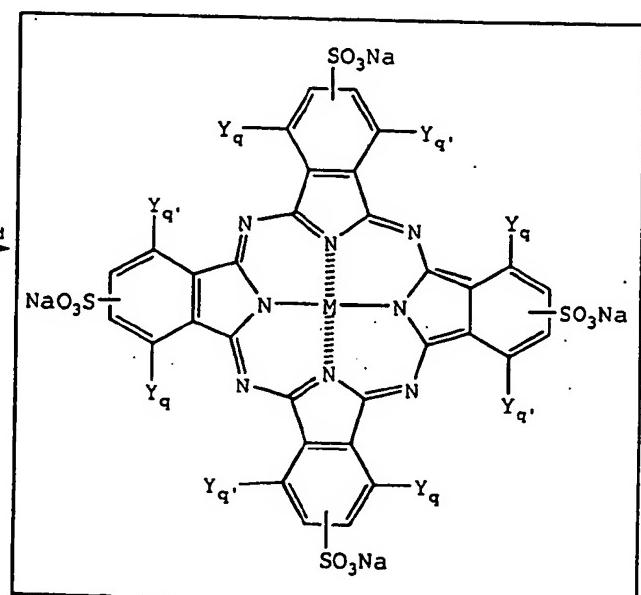
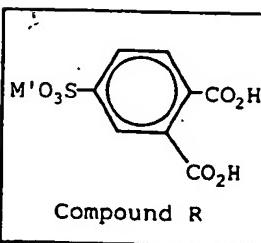
35

40

45

50

55

 $\delta/\text{or}$  $M-(Y)_d$  $M-(Y)_d$ 

[0066] In the formulae above,  $X_p$  corresponds to  $X_{11}, X_{12}, X_{13}$  or  $X_{14}$  in formula (II) and  $Y_q$  and  $Y_{q'}$  each corresponds to  $Y_{11}, Y_{12}, Y_{13}, Y_{14}, Y_{15}, Y_{16}, Y_{17}$  or  $Y_{18}$  in formula (II). In Compound R,  $M'$  represents cation. Examples of the cation represented by  $M'$  include alkali metal ion such as Li, Na and K, and organic cation such as triethylammonium ion and

pyridinium ion.

5                   Formula (III):



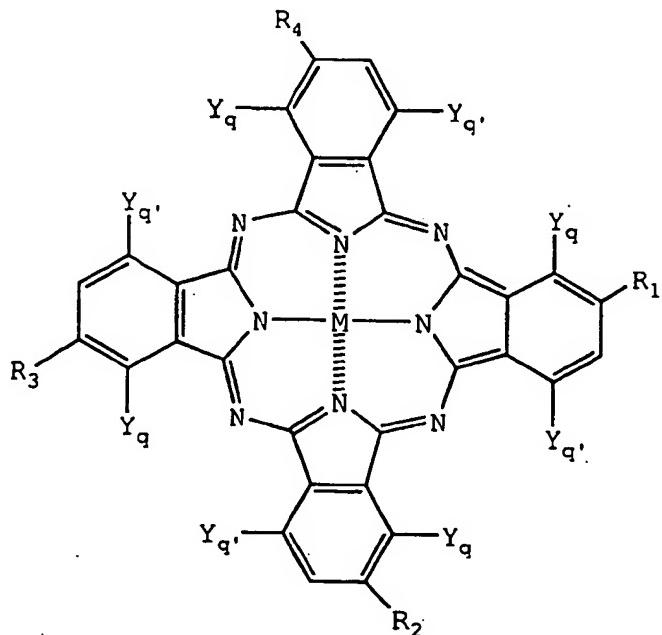
wherein M has the same meaning as M in formulae (I) and (II), Y represents a monovalent or divalent ligand such as halogen atom, acetate anion, acetylacetone and oxygen, and d represents an integer of 1 to 4.

10 [0067] That is, according to this synthesis method, a specific number of desired substituents can be introduced. Particularly, in the case of introducing a large number of electron withdrawing groups so as to render the oxidation potential nobler as in the present invention, this synthesis method is very excellent as compared with the above-described method for synthesizing the phthalocyanine compound of formula (I).

15 [0068] The thus-obtained phthalocyanine compound represented by formulae (II) is usually a mixture of compounds represented by the following formulae (a)-1 to (a)-4 which are isomers in respect to the substitution site of each  $X_p$ , namely, a  $\beta$ -position substitution type.

20

Formula (a)-1:



50

55

## Formula (a)-2:

5

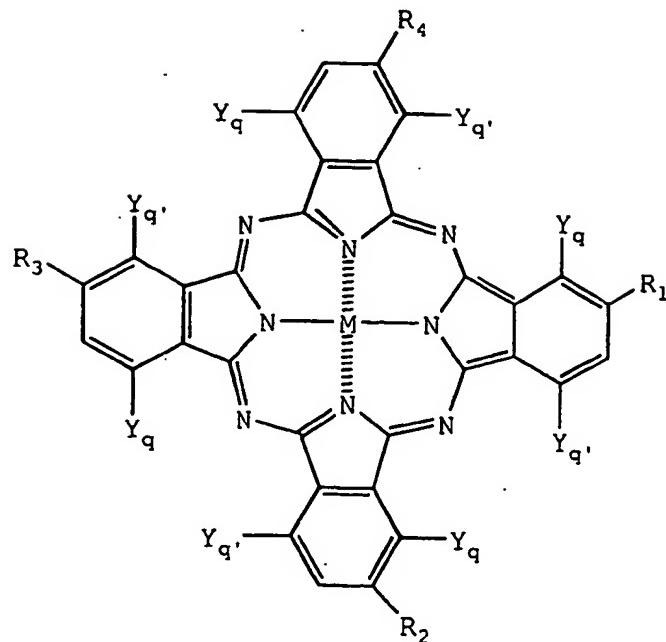
10

15

20

25

30



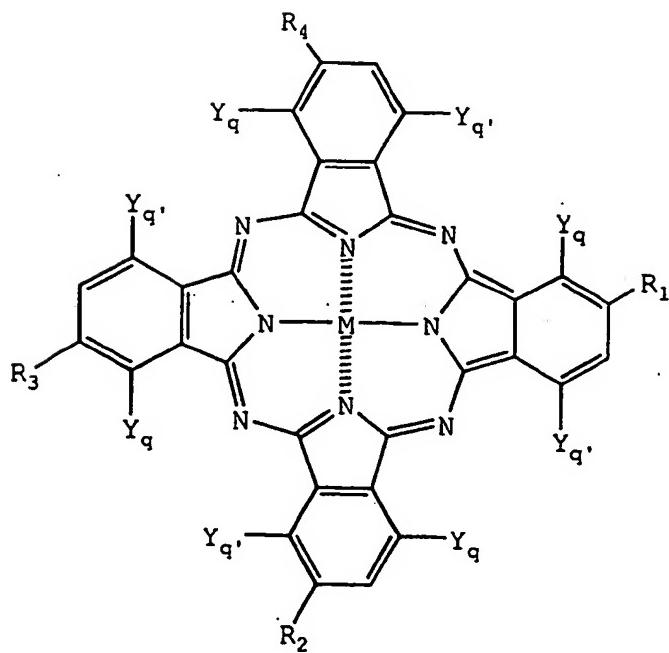
35

40

45

50

55



## Formula (a)-4:

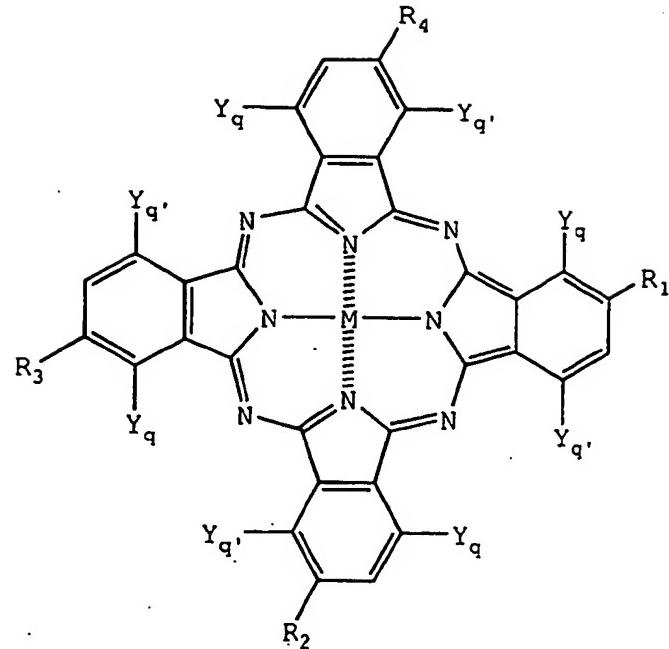
5

10

15

20

25



[0069] In the synthesis method above, when all Xp are the same, a  $\beta$ -position substitution type phthalocyanine dye where  $X_{11}$ ,  $X_{12}$ ,  $X_{13}$  and  $X_{14}$  are completely the same substituents can be obtained. On the other hand, when Xp are different, a dye having substituents of the same kind but partially different from each other or a dye having substituents different from each other can be synthesized. Among the dyes of formula (II), these dyes having electron withdrawing substituents different from each other are preferred because the solubility and aggregating property of dye and the aging stability of ink can be controlled.

[0070] In the present invention, it has been found very important in any substitution type for the improvement of fastness that the oxidation potential is nobler than 1.0 V (vs SCE). The great effect thereof cannot be expected at all from the above-described known techniques. Furthermore, although the cause is not particularly known, there is a tendency that the  $\beta$ -position substitution type is apparently more excellent in the color, light fastness, ozone resistance and the like than the  $\alpha,\beta$ -position mixed substitution type.

[0071] Specific examples (Compounds I-1 to I-12 and 101 to 190) of the phthalocyanine dyes represented by formulae (I) and (II) are set forth below, however, the phthalocyanine dye for use in the present invention is not limited to the following examples.

45

50

55

Compounds:

[0072]

5

10

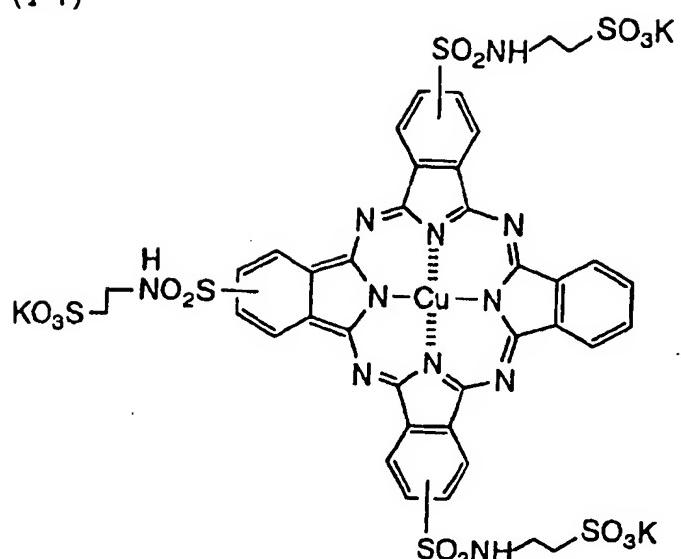
15

20

25

30

(I-1)



35

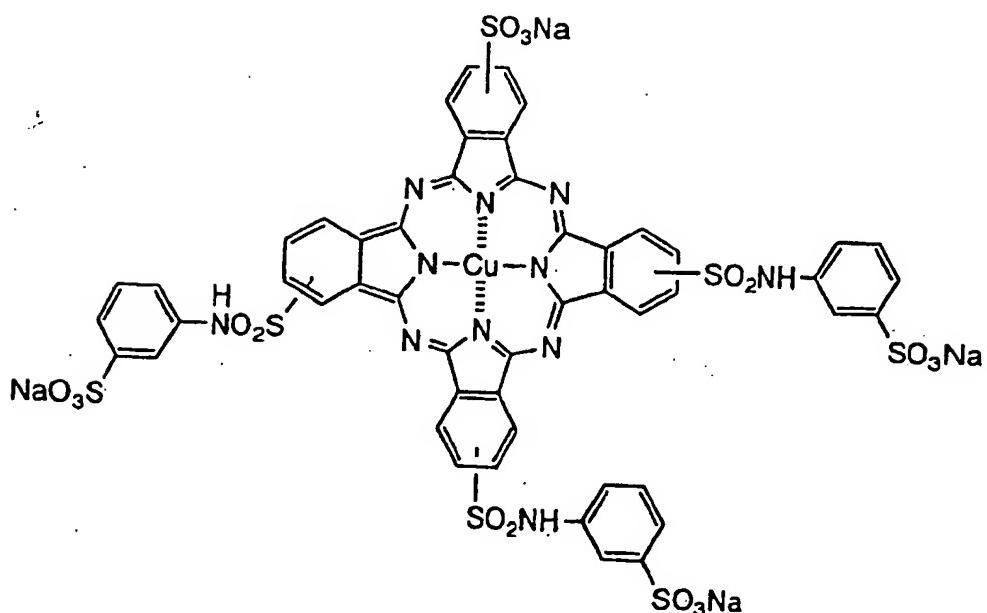
40

45

50

55

(I-2)



5

(I-3)

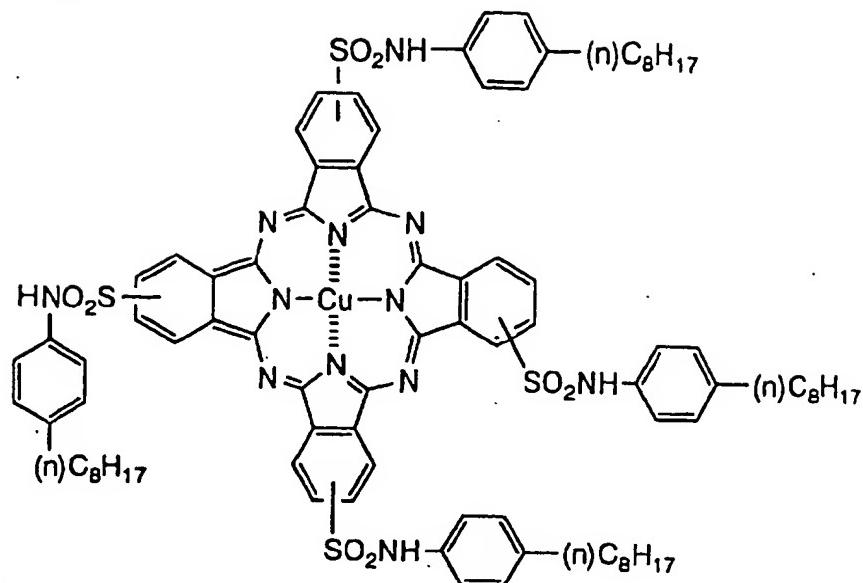
10

15

20

25

30



35

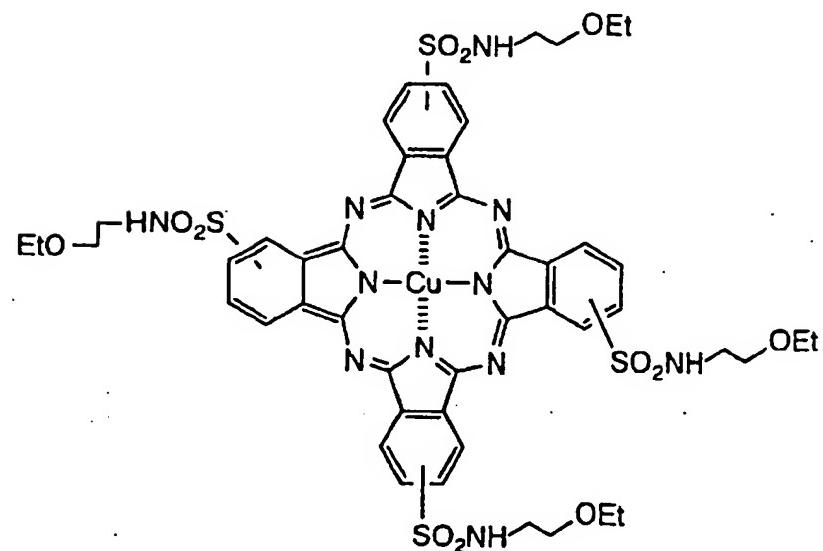
40

45

50

55

(I-4)



5

(I-5)

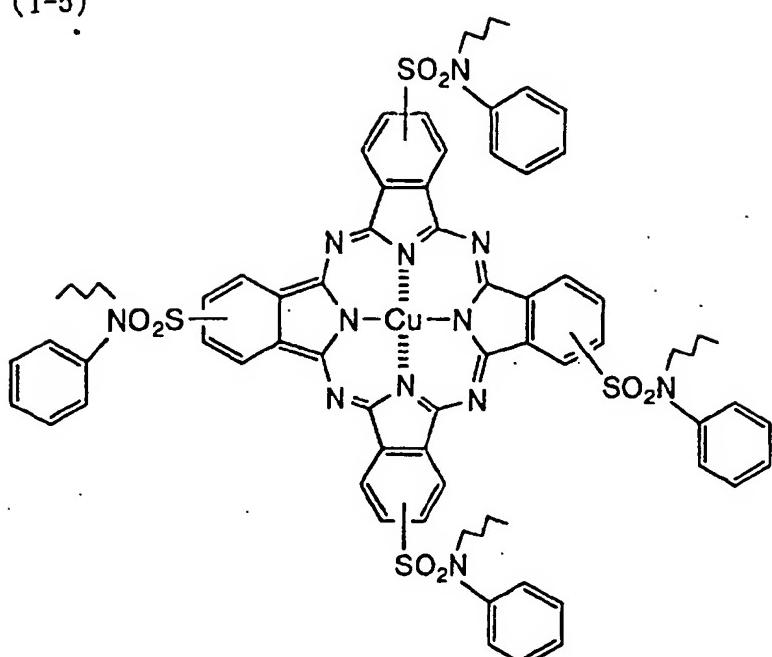
10

15

20

25

30



35

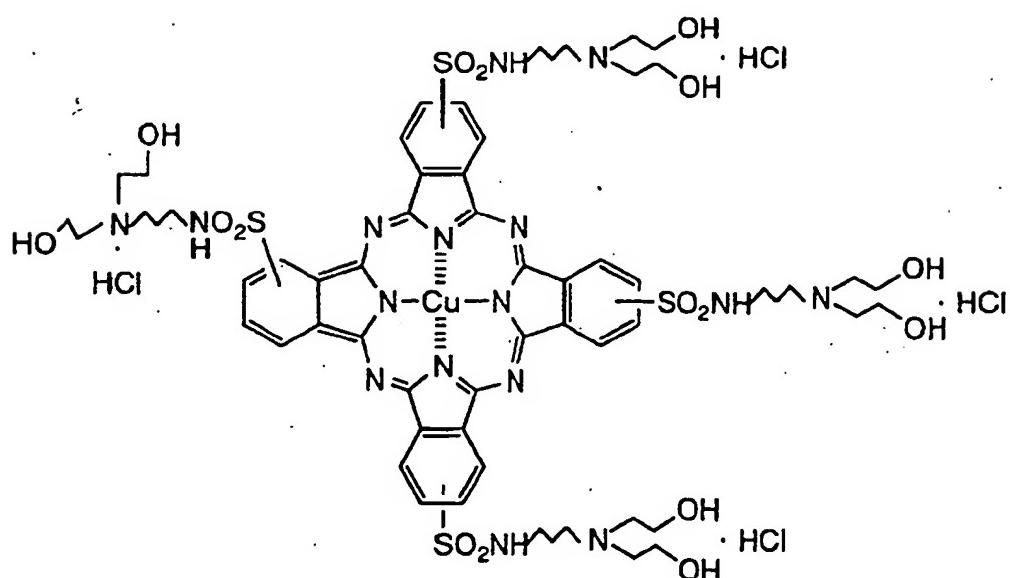
40

45

50

55

(I-6)



5

(I-7)

10

15

20

25

30

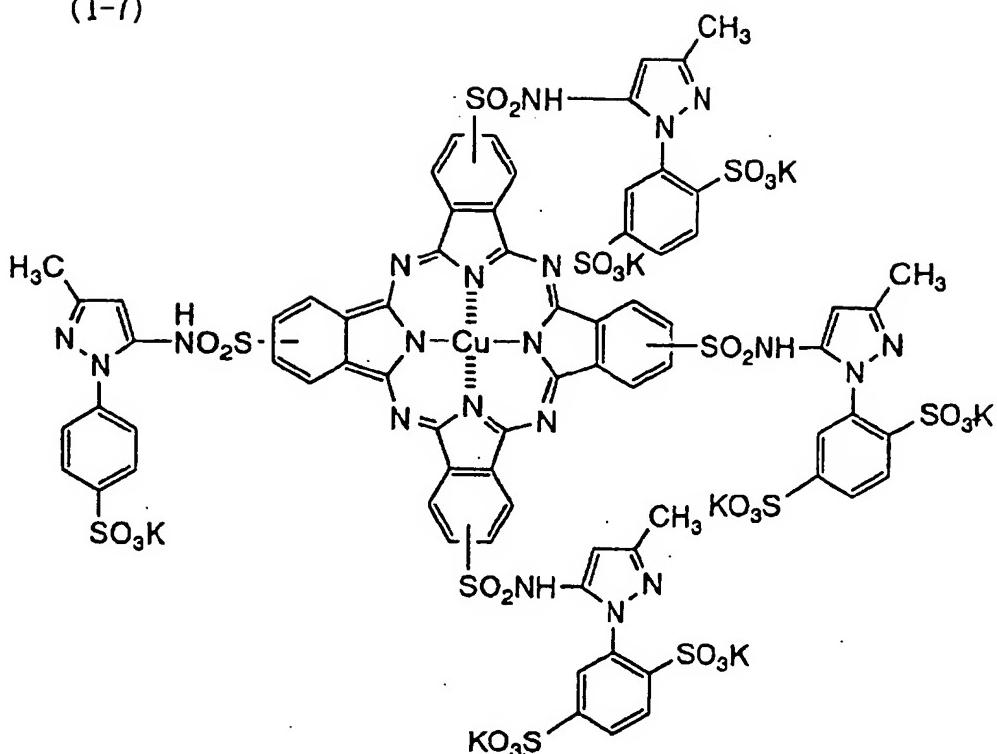
35

40

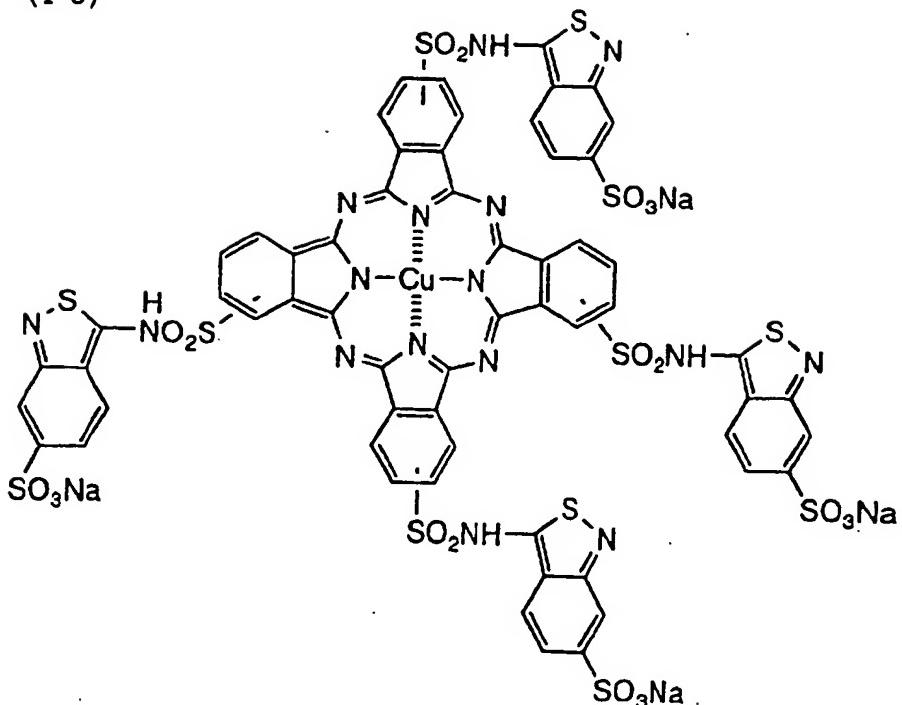
45

50

55



(I-8)



5

(I-9)

10

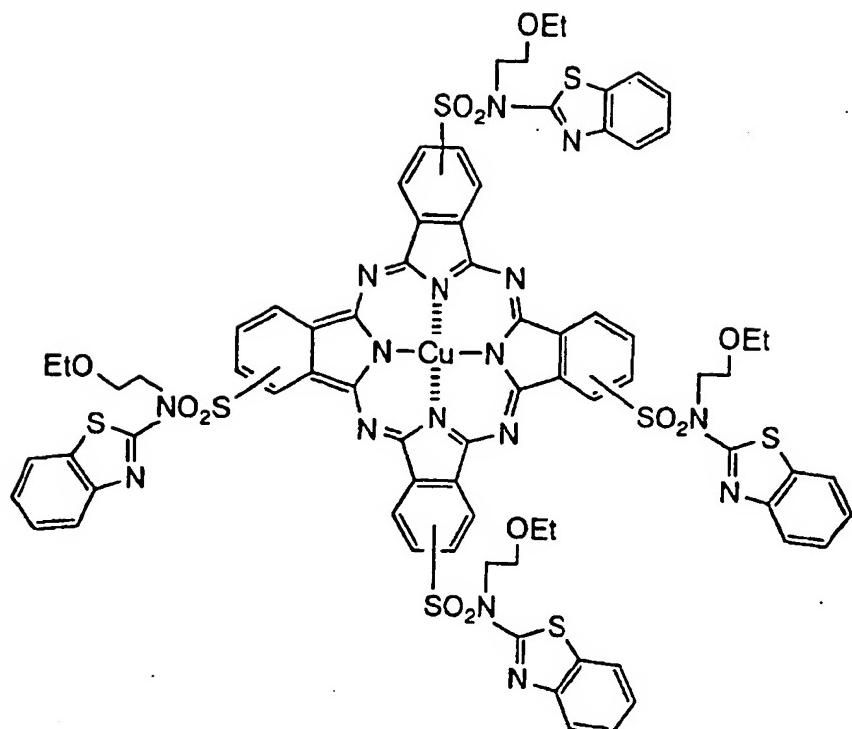
15

20

25

30

35



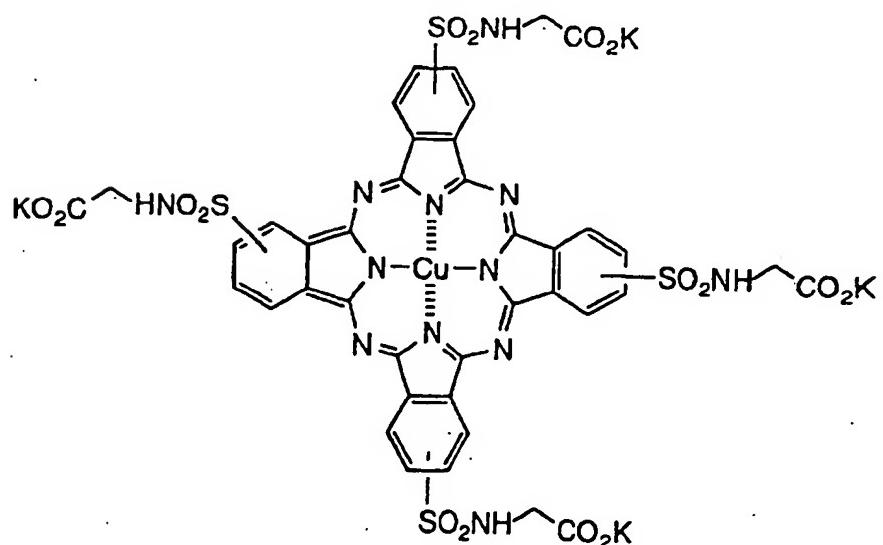
40

45

50

55

(I-10)



5

(I-11)

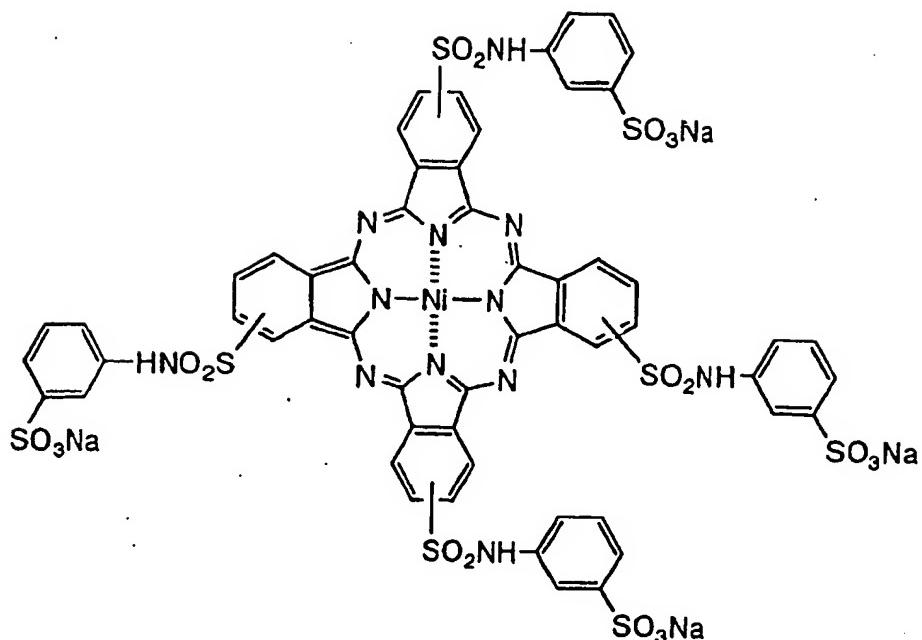
10

15

20

25

30



35

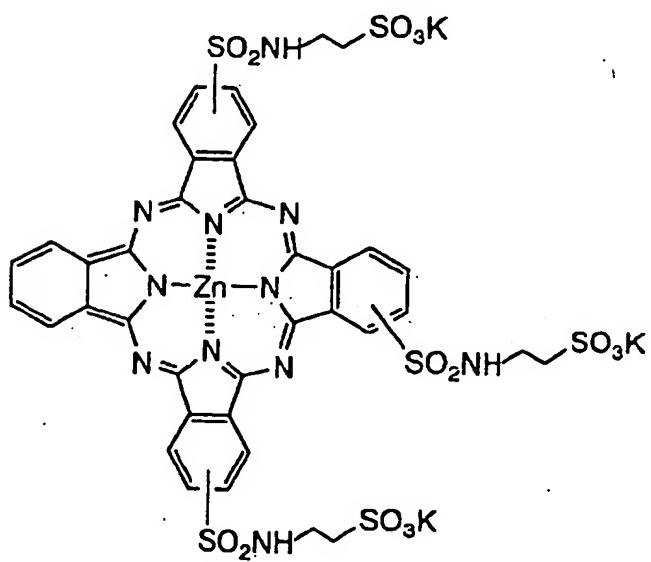
40

45

50

55

(I-12)



[0073] In the following Tables, specific examples of each pair of (X<sub>1</sub>, X<sub>2</sub>), (Y<sub>11</sub>, Y<sub>12</sub>), (Y<sub>13</sub>, Y<sub>14</sub>), (Y<sub>15</sub>, Y<sub>16</sub>) and (Y<sub>17</sub>,

Y<sub>18</sub>) are independently in an irregular order.

**5**

**10**

**15**

**20**

**25**

**30**

**35**

**40**

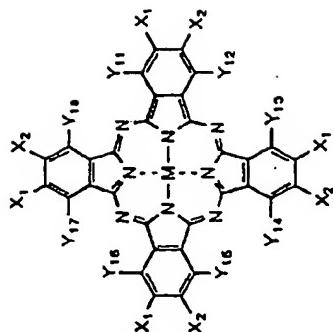
**45**

**50**

**55**

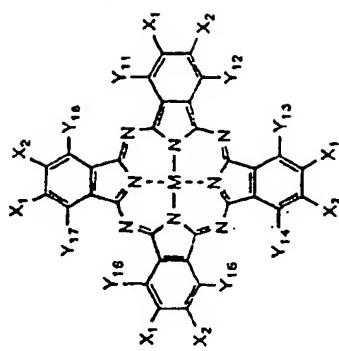
**21**

[Table 1]



No.	M	X <sub>1</sub>	X <sub>2</sub>	Y <sub>11</sub> , Y <sub>12</sub>	Y <sub>13</sub> , Y <sub>14</sub>	Y <sub>15</sub> , Y <sub>16</sub>	Y <sub>11</sub> , Y <sub>16</sub>
101	Cu	-SO <sub>2</sub> -NH-CH <sub>2</sub> -CH <sub>2</sub> -SO <sub>3</sub> Li		-H	-H, -H	-H, -H	-H, -H
102	Cu	-SO <sub>2</sub> -NH-CH <sub>2</sub> -CH-CO-NH-CH <sub>2</sub> CH <sub>2</sub> -SO <sub>3</sub> Na	OH	-H	-Cl, -H	-Cl, -H	-Cl, -H
103	Cu	-SO <sub>2</sub> -NH-CH <sub>2</sub> -CH <sub>2</sub> -SO <sub>2</sub> NH-CH <sub>2</sub> CH <sub>2</sub> -SO <sub>3</sub> Li	OH	-H	-H, +H	-H, -H	-H, -H
104	Cu	-SO <sub>2</sub> -NH-		-H	-H, +H	-H, -H	-H, -H
105	Ni	-SO <sub>2</sub> -NH-CH <sub>2</sub> -CH <sub>2</sub> -CO-NH-CH-COONa	CH <sub>2</sub> -COO <sup>-</sup> Na	-H	-Cl, -H	-Cl, -H	-Cl, -H
106	Cu	-SO <sub>2</sub> -NH-CH <sub>2</sub> -CH <sub>2</sub> -SO <sub>2</sub> -NH-CH-COOI	CH <sub>2</sub> -OH	-CN	-H, +H	-H, -H	-H, -H
107	Cu	-SO <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -SO <sub>2</sub> -NH-CH-COOI		-H	-H, +H	-H, -H	-H, -H
108	Cu	-SO <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -SO <sub>2</sub> -NH-CH <sub>2</sub> -SO <sub>3</sub> Li		-H	-H, +H	-H, -H	-H, -H
109	Cu	-SO <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -SO <sub>3</sub> K		-H	-H, -H	-H, -H	-H, -H
110	Cu	-SO <sub>2</sub> -(CH <sub>2</sub> ) <sub>5</sub> -CO <sub>2</sub> K		-H	-H, +H	-H, -H	-H, -H

[Table 2]



No.	M	X <sub>1</sub>	X <sub>2</sub>	Y <sub>11</sub> , Y <sub>12</sub>	Y <sub>13</sub> , Y <sub>14</sub>	Y <sub>15</sub> , Y <sub>16</sub>	Y <sub>17</sub> , Y <sub>18</sub>
111	Cu	-SO <sub>2</sub> -NH-CH <sub>2</sub> -CH <sub>2</sub> -SO <sub>2</sub> -NH-CH <sub>2</sub> CH <sub>2</sub> -CH <sub>2</sub> -SO <sub>3</sub> Li	OH	-H	-H, -H	-H, -H	-H, -H
112	Cu	-SO <sub>2</sub> -NH-CH <sub>2</sub> -CH <sub>2</sub> -SO <sub>2</sub> NH-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -SO <sub>3</sub> Li	OH	-H, -H	-H, -H	-H, -H	-H, -H
113	Cu	-SO <sub>2</sub> -CH <sub>2</sub> -CH-CH <sub>2</sub> SO <sub>3</sub> K	OH	-H	-H, -H	-H, -H	-H, -H
114	Cu	-SO <sub>2</sub> -CH <sub>2</sub> -CH-CH <sub>2</sub> CH <sub>2</sub> OH	CH <sub>3</sub>	-SO <sub>3</sub> Li	-H, -H	-H, -H	-H, -H
115	Cu	-SO <sub>2</sub> NH(CH <sub>2</sub> ) <sub>3</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub> · CH <sub>3</sub> —	OH	-H	-H, -H	-H, -H	-H, -H
116	Cu	-CO-NH-CH <sub>2</sub> -CH-CH <sub>2</sub> SO <sub>3</sub> K	COOJ	-H	-H, -H	-H, -H	-H, -H
117	Cu	-CO-NH-CH-CH <sub>2</sub> SO <sub>3</sub> Li		-H	-H, -H	-H, -H	-H, -H

[Table 3]

5

10

15

20

25

30

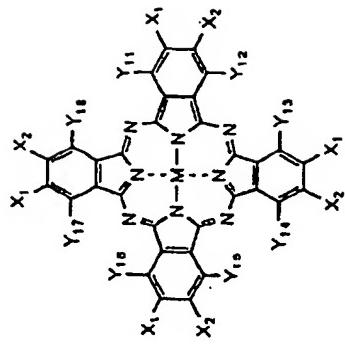
35

40

45

50

55



No.	M	$X_1$	$X_2$	$Y_{11}, Y_{12}$	$Y_{13}, Y_{14}$	$Y_{15}, Y_{16}$	$Y_{17}, Y_{18}$
118	Cu	$-SO_2CH_2CH_2CH_2CH_2SO_3Na$	-H	-H, -H	-H, -H	-H, -H	-H, -H
119	Cu	$-SO_2-CH_2-CH-CH_2-SO_3Na$	-H	-H, -H	-H, -H	-H, -H	-H, -H
120	Cu	$-SO_2-CH_2-CH_2-CH-COOLi$	-H	-H, -H	-H, -H	-H, -H	-H, -H
121	Cu	$-SO_2(CH_2)_3SO_2NHCH_2-CH-CH_2-SO_3Li$	-H	-H, -H	-H, -H	-H, -H	-H, -H
122	Cu	$-CO_2CH_2CH_2CH_2SO_2-NH-CH_2-CH-CH_2-SO_3Li$	-H	-H, -H	-H, -H	-H, -H	-H, -H
123	Cu	$-SO_2NH-C_6H_4(t)$	-H	-H, -H	-H, -H	-H, -H	-H, -H
124	Cu	$-SO_2-NH-CH_2-CH-CH_2CHCH_2-CH_2$	-H	-H, -H	-H, -H	-H, -H	-H, -H

5

[Table 4]

10

15

20

25

30

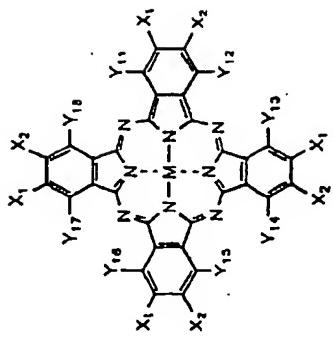
35

40

45

50

55



No.	M	X <sub>1</sub>	X <sub>2</sub>	Y <sub>11</sub> , Y <sub>12</sub>	Y <sub>13</sub> , Y <sub>14</sub>	Y <sub>15</sub> , Y <sub>16</sub>	Y <sub>17</sub> , Y <sub>18</sub>
125	Cu	CH <sub>3</sub>	-H	-H, -H	-H, -H	-H, -H	-H, -H
126	Cu	CH <sub>3</sub>	-H	-H, -H	-H, -H	-H, -H	-H, -H
127	Cu	-SO <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SO <sub>2</sub> NHCH <sub>2</sub> CH <sub>2</sub> O-CH <sub>2</sub> CH <sub>3</sub>	-H	-H, -H	-H, -H	-H, -H	-H, -H
128	Zn	O-CH <sub>3</sub>	-CN	-H, -H	-H, -H	-H, -H	-H, -H
129	Cu	CH <sub>2</sub> CH <sub>3</sub>	-H	-Cl, -H	-Cl, -H	-Cl, -H	-Cl, -H
130	Cu	CH <sub>3</sub>	-H	-H, -H	-H, -H	-H, -H	-H, -H
131	Cu	-CO <sub>2</sub> -CH-CH <sub>2</sub> -O-C <sub>4</sub> H <sub>9</sub> (I)	-H	-H	-H, -H	-H, -H	-H, -H
		CH <sub>3</sub>	SO <sub>3</sub> <sup>2-</sup>				

5

10

15

20

25

30

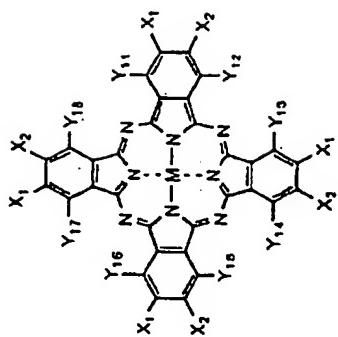
35

40

45

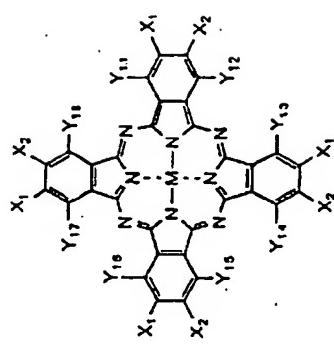
50

55



No.	M	X <sub>1</sub>	X <sub>2</sub>	Y <sub>11</sub> , Y <sub>12</sub>	Y <sub>13</sub> , Y <sub>14</sub>	Y <sub>15</sub> , Y <sub>16</sub>	Y <sub>17</sub> , Y <sub>18</sub>
132	Cu	$\text{CO}_2\text{C}_8\text{H}_{13}(n)$ $\text{CO}_2\text{C}_8\text{H}_{13}(n)$	-H	-H, -H	-H, -H	-H, -H	-H, -H
133	Cu	$-\text{SO}_2\text{NH}-\text{C}_6\text{H}_4-\text{OCH}_2\text{CH}_2\text{OCH}_3$ $\text{SO}_2\text{NHCH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{C}_2\text{H}_5$	-H	-H, -H	-H, -H	-H, -H	-H, -H
134	Cu	$-\text{SO}_2\text{NH}-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_3$ $\text{CH}_2\text{CH}_3$	-H	-H, -H	-H, -H	-H, -H	-H, -H
135	Cu	$-\text{SO}_2-\text{C}_6\text{H}_4-\text{CO}_2\text{Na}$ $\text{C}_4\text{H}_9(n)$	-H	-H, -H	-H, -H	-H, -H	-H, -H
136	Cu	$-\text{SO}_2\text{N}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_5$	-H	-H, -H	-H, -H	-H, -H	-H, -H

[Table 6]



No.	M	$X_1$	$X_2$	$Y_{11}, Y_{12}$	$Y_{13}, Y_{14}$	$Y_{15}, Y_{16}$	$Y_{17}, Y_{18}$
137	Cu	$-SO_3Li$	-H	-H, -H	-H, -H	-H, -H	-H, -H
138	Cu	$CH_3$ $-SO_2NH$ $LiO_3S$	-H	-H, -H	-H, -H	-H, -H	-H, -H
139	Cu	$CO_2Li$ $-NH-C(=O)-C_6H_4-CO_2Li$	-Cl	-H, -H	-H, -H	-H, -H	-H, -H
140	Cu	$NH-CH_2-CH_2-CH_2-SO_3Li$ $CH_3$ $-CO_2-CH_2CH_2CH_2-NH-$ $N=N$ $NH-CH_2-CH_2-CH_2-SO_3Li$ $CH_3$	-H	-H, -H	-H, -H	-H, -H	-H, -H

5

10

15

20

25

30

35

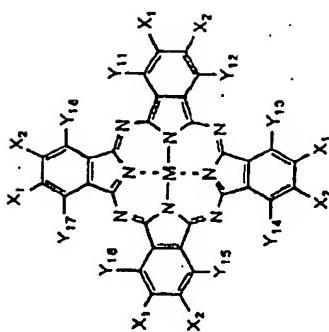
40

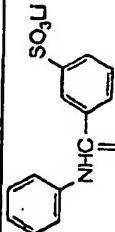
45

50

55

[Table 7]



No.	M	X <sub>1</sub>	X <sub>2</sub>	Y <sub>11</sub> , Y <sub>12</sub>	Y <sub>13</sub> , Y <sub>14</sub>	Y <sub>15</sub> , Y <sub>16</sub>	Y <sub>17</sub> , Y <sub>18</sub>
141	Cu	COONa —SO <sub>2</sub> NH—CH—CH <sub>2</sub> —CO—N—(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub>	-H	-H, -H	-H, -H	-H, -H	-H, -H
142	Cu	—SO <sub>2</sub> NH— 	-H	-H, -H	-H, -H	-H, -H	-H, -H
143	Cu	OH COOK	-H	-H, -H	-H, -H	-H, -H	-H, -H
144	Cu	—CO—NH—CH <sub>2</sub> CH <sub>2</sub> —NH—CO— 	-H	-H, -H	-H, -H	-H, -H	-H, -H
145	Cu	—SO <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> SO <sub>3</sub> U	-H	-H, -H	-H, -H	-H, -H	-H, -H

[0074] In the following Tables, each introduction site of substituents ( $R_1$ ) and ( $R_2$ ) is in an irregular order within the  $\beta$ -position substitution type.

**5**

**10**

**15**

**20**

**25**

**30**

**35**

**40**

**45**

**50**

**55**

[Table 8]

M-Pc(R <sub>1</sub> ) <sub>n</sub> (R <sub>2</sub> ) <sub>c</sub>	No.	M	R <sub>1</sub>	m	R <sub>2</sub>	n
	146	Cu	—SO <sub>2</sub> —NH—CH <sub>2</sub> —CH—SO <sub>3</sub> Li	3	—SO <sub>2</sub> —NH—CH <sub>2</sub> —CH—CH <sub>3</sub>	1
	147	Cu	—SO <sub>2</sub> —NH—CH <sub>2</sub> —CH—SO <sub>3</sub> Li	3	—SO <sub>2</sub> —NH—CH <sub>2</sub> —CH <sub>2</sub> —SO <sub>2</sub> —NH—CH <sub>2</sub> —CH—CH <sub>3</sub>	—OH
	148	Cu	—SO <sub>2</sub> —NH—CH <sub>2</sub> —CH—SO <sub>3</sub> Li	3	—SO <sub>2</sub> —NH—CH <sub>2</sub> —CH <sub>2</sub> —SO <sub>2</sub> —NH—CH <sub>2</sub> —CH <sub>2</sub> —O—CH <sub>2</sub> —CH <sub>2</sub> —OH	1
	149	Cu	—SO <sub>2</sub> —NH—CH <sub>2</sub> —CH—SO <sub>3</sub> Li	2	—SO <sub>2</sub> —NH—CH <sub>2</sub> —CH <sub>2</sub> —CO—N—(CH <sub>2</sub> —CH <sub>2</sub> —OH) <sub>2</sub>	2
	150	Cu	—SO <sub>2</sub> —NH—CH <sub>2</sub> —CH <sub>2</sub> —SO <sub>2</sub> —NH—CH <sub>2</sub> —CH <sub>2</sub> —COONa	3	—SO <sub>2</sub> —NH—CH <sub>2</sub> —CH <sub>2</sub> —O—CH <sub>2</sub> —CH <sub>2</sub> —OH	1
	151	Cu	—SO <sub>2</sub> —NH—  —SO <sub>2</sub> NH—CH <sub>2</sub> —CH—SO <sub>3</sub> Li	3	—SO <sub>2</sub> —NH—CH <sub>2</sub> —CH <sub>2</sub> —O—CH <sub>2</sub> —CH <sub>2</sub> —OH	—
	152	Cu	—SO <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH—SO <sub>3</sub> Li	2.5	—SO <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —O—CH <sub>2</sub> —CH <sub>2</sub> —OH	1.5
	153	Cu	—SO <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH—SO <sub>3</sub> Na	2	—SO <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CO—N—(CH <sub>2</sub> —CH <sub>2</sub> —OH) <sub>2</sub>	2
	154	Cu	—SO <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —SO <sub>3</sub> Li	3	—SO <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —SO <sub>2</sub> —NH—CH <sub>2</sub> —CH—CH <sub>3</sub>	1
	155	Cu	—SO <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —COOK	2	—SO <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —SO <sub>2</sub> —NH—CH <sub>2</sub> —CH—CH <sub>3</sub>	2
	156	Cu	—SO <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —SO <sub>3</sub> Li	3	—SO <sub>2</sub> —CH <sub>2</sub> —CH—CH <sub>2</sub> —SO <sub>3</sub> Li	1
	157	Cu	—SO <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —O—CH <sub>2</sub> —SO <sub>3</sub> Li	2	—SO <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CO <sub>2</sub> —CH <sub>2</sub> —CH—CH <sub>2</sub> —COOK	2

[Table 9]

$N\text{-Pc}(R_1)_m(R_2)_n$					
No.	M	$R_1$	$\pi$	$R_2$	c
158	Cu	$-\text{SO}_2-\text{CH}_2-\overset{\text{OH}}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{SO}_3\text{Li}$	3	$-\text{SO}_2-\text{CH}_2-\text{C}_6\text{H}_4-\text{SO}_2\text{NH}-\text{CH}_2-\overset{\text{OH}}{\underset{ }{\text{CH}}}=\text{CH}_2-\text{OH}$	1
159	Cu	$-\text{SO}_2\text{NHCH}_2\text{CH}_2-\text{SO}_3\text{Li}$	3	$-\text{SO}_2-\text{CH}_2-\text{CH}_2-\text{SO}_2-\text{NH}-\text{CH}_2-\overset{\text{OH}}{\underset{ }{\text{CH}}}=\text{CH}_2-\text{CH}_3$	1
160	Cu	$-\text{SO}_2-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\underset{ }{\text{CH}}}=\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{SO}_3\text{Na}$	3	$-\text{SO}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\overset{\text{COONa}}{\underset{ }{\text{CO}}}=\text{N}-\text{CH}_2-\text{COONa}$	1
161	Cu	$-\text{SO}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{NHCH}_2-\text{CH}_2-\text{CH}_2\text{SO}_3\text{Li}$	3	$-\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{NHCH}_2-\text{CH}_2-\overset{\text{OH}}{\underset{ }{\text{CH}}}=\text{CH}_2\text{SO}_3\text{Li}$	1
162	Cu	$-\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Li}$	2	$-\text{SO}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$	2
163	Cu	$-\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{K}$	3	$-\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{NH}-\text{CH}_2-\overset{\text{CH}_3}{\underset{ }{\text{CH}}}=\text{CH}_2-\text{OH}$	1
164	Cu	$-\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Li}$	2	$-\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{N}(\text{CH}_2\text{CH}_2\text{O})_2$	2
165	Cu	$-\text{CO}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{SO}_3\text{K}$	3	$-\text{CO}-\text{NH}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\underset{ }{\text{CH}}}=\text{CH}_2-\text{CH}_2-\text{OH}$	1
166	Cu	$-\text{CO}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{SO}_3-\text{NH}-\text{CH}_2-\text{CH}_2-\text{COONa}$	3	$-\text{CO}-\text{NH}-\text{CH}_2-\overset{\text{OH}}{\underset{ }{\text{CH}}}=\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}-\text{N}(\text{CH}_2-\text{CH}_2-\text{OH})_2$	1
167	Cu	$-\text{SO}_2(\text{CH}_2)_3\text{SO}_2\text{NHCH}_2-\text{CH}_2-\text{CH}_2\text{CO}_2\text{Li}$	2.5	$-\text{CO}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}-\text{N}(\text{CH}_2-\text{CH}_2-\text{OH})_2$	1.5
168	Cu	$-\text{CO}_2-\text{CH}_2-\overset{\text{CH}_3}{\underset{ }{\text{CH}}}=\text{CH}_2-\text{CH}_2-\text{CO}-\text{N}(\text{CH}_2-\text{CH}_2-\text{OH})_2$	2	$-\text{CO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}-\text{N}(\text{CH}_2-\text{CH}_2-\text{OH})_2$	2
169	Cu	$-\text{CO}_2-\text{CH}_2-\text{CH}_2-\overset{\text{OH}}{\underset{ }{\text{CH}}}=\text{CH}_2-\text{SO}_3\text{Li}$	3	$-\text{CO}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{SO}_2-\text{NH}-\text{CH}_2-\overset{\text{OH}}{\underset{ }{\text{CH}}}=\text{CH}_2-\text{CH}_3$	1
170	Cu	$-\text{CO}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOK}$	2	$-\text{CO}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{SO}_2-\text{NH}-\text{CH}_2-\overset{\text{OH}}{\underset{ }{\text{CH}}}=\text{CH}_2-\text{COOK}$	2

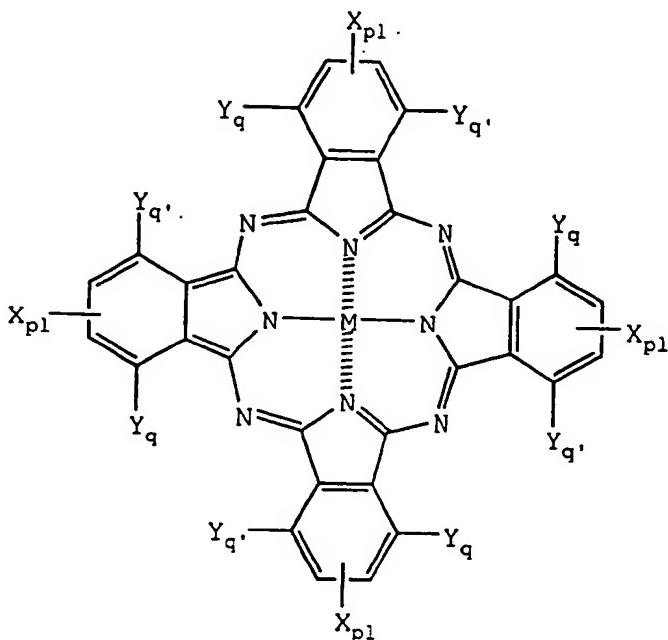
[Table 10]

M-Pe(R) <sub>m</sub> (R' <sub>n</sub> )	No.	M	R <sub>1</sub>	R <sub>2</sub>	m	n
171 Cu -CO <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -SO <sub>3</sub> Na					3	-CO <sub>2</sub> -CH <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -SO <sub>2</sub> NH-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH
172 Cu -SO <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> O-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> SO <sub>3</sub> K					2	-CO <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CO <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -COOK
173 Cu -SO <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> SO <sub>2</sub> NHC <sub>6</sub> H <sub>4</sub> C <sub>6</sub> H <sub>4</sub> OH					2	-CO <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -SO <sub>3</sub> Li
174* Cu -SO <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> SO <sub>2</sub> NHCH <sub>2</sub> -CH <sub>2</sub> SO <sub>3</sub> K					3	-CO <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CO-N-CH <sub>2</sub> -NH-CH <sub>2</sub> -CH <sub>2</sub> -COOLi
175 Cu -SO <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> SO <sub>2</sub> NH(CH <sub>3</sub> ) <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub> OH					2	-SO <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -SO <sub>2</sub> -NH-CH <sub>2</sub> -CH-C <sub>6</sub> H <sub>4</sub> -CH <sub>3</sub>
176 Cu -SO <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -SO <sub>2</sub> -NH-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>					3	-SO <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -SO <sub>2</sub> -NH-CH <sub>2</sub> -CH-C <sub>6</sub> H <sub>4</sub> -CH <sub>3</sub>
177 Cu -SO <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>3</sub>					2	-SO <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -SO <sub>2</sub> -NH-CH <sub>2</sub> -CH-C <sub>6</sub> H <sub>4</sub> -CH <sub>3</sub>
178 Cu -SO <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -OH					3	-SO <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CO <sub>2</sub> -CH <sub>2</sub> -CH-C <sub>6</sub> H <sub>4</sub> -CH <sub>3</sub>
179 Cu -SO <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>3</sub>					2	-SO <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -SO <sub>2</sub> -NH-CH <sub>2</sub> -CH-C <sub>6</sub> H <sub>4</sub> -CH <sub>3</sub>
180 Cu -SO <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>3</sub>					3	-SO <sub>2</sub> NH-CH <sub>2</sub> -CH <sub>2</sub> -SO <sub>2</sub> NH-CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH-C <sub>6</sub> H <sub>4</sub> -CH <sub>3</sub>
181 Cu -SO <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CO <sub>2</sub> -NH-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>					3	-SO <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -SO <sub>2</sub> -NH-CH <sub>2</sub> -CH-C <sub>6</sub> H <sub>4</sub> -CH <sub>3</sub>
182 Cu -SO <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -SO <sub>2</sub> NH-CH <sub>2</sub> -CH-CH <sub>3</sub>					2.5	-SO <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CO <sub>2</sub> -NH-CH <sub>2</sub> -CH-C <sub>6</sub> H <sub>4</sub> -CH <sub>3</sub>

[Table 11]

M-Pc(R) <sub>m</sub> (R' <sub>n</sub> ) <sub>n</sub>	No.	M	R <sub>1</sub>	m	R <sub>2</sub>	n
183 Cu $-SO_2-CH_2-CH_2-CO_2-NH-CH_2-CH_2-CH_3$			CH <sub>3</sub>	2	$-SO_2-CH_2-CH_2-SO_2-NH-(CH_2)_3-CH_2-O-CH_2-CH_2-OH$	2
184 Cu $-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH_2-CH_2-OH$			OH	3	$-SO_2-CH_2-CH_2-O-CH_2-CH_2-O-CH_2$	1
185 Cu $-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH_2-CH_2-OH$			OH	3	$-SO_2-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_2$	1
186 Cu $-SO_2-CH_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH_2-CH_2-OH$			CH <sub>3</sub>	3	$-SO_2-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_2$	1
187 Cu $-SO_2-CH_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH_2-CH_2-CH_2-OH$			CH <sub>3</sub>	3	$-CO_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$	1
188 Cu $-CO_2-CH_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH_2-CH_2-OH$			CH <sub>3</sub>	3	$-CO_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$	1
189 Cu $-CO-NH-CH_2-CH_2-SO_2-NH-CH_2-CH_2-CH_2-OH$			CH <sub>3</sub>	3	$-SO_2-NH-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$	1
190 Cu $-CO-NH-CH_2-CH_2-CH_2-CH_2-CH_2-OH$			CH <sub>3</sub>	3	$-CO-NH-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-OH$	1

[0075] The structural formula of the phthalocyanine compound represented by M-Pc( $X_{p1}$ )<sub>m</sub>( $X_{p2}$ )<sub>n</sub> in Tables 8 to 11 is shown below:



(wherein each  $X_{p1}$  is independently  $X_{p1}$  or  $X_{p2}$ ).

[0076] The phthalocyanine dye represented by formula (I) can be synthesized according to the patent publications described above. Furthermore, the phthalocyanine dye represented by formula (II) can be synthesized by the methods described in JP-A-2001-226275, JP-A-2001-96610, JP-A-2001-47013 and JP-A-2001-193638. The starting material, dye intermediate and synthesis route are not limited to those described in these patent publications.

[0077] The inkjet recording ink of the present invention contains the above-described phthalocyanine dye in an amount of preferably from 0.2 to 20 % by weight, more preferably from 0.5 to 15 % by weight.

[0078] In combination with the above-described cyan dye, other dyes may be used in the inkjet recording ink of the present invention so as to adjust the color tone for obtaining a full color image. Examples of the dye which can be used in combination include the followings.

[0079] Examples of the yellow dye include aryl- or heteryl-azo dyes having a phenol, a naphthol, an aniline, a pyrazolone, a pyridone or an open chain-type active methylene compound as the coupling component; azomethine dyes having an open chain-type active methylene compound as the coupling component; methine dyes such as benzylidene dye and monomethine oxonol dye; and quinone-base dyes such as naphthoquinone dye and anthraquinone dye. Other examples of the dye species include quinophthalone dye, nitro-nitroso dye, acridine dye and acridinone dye. These dyes may be a dye which provides a yellow color for the first time when a part of the chromophore is dissociated. In this case, the counter cation may be an inorganic cation such as alkali metal and ammonium, an organic cation such as pyridinium and quaternary ammonium salt, or a polymer cation having such a cation as a partial structure.

[0080] Examples of the magenta dye include aryl- or heteryl-azo dyes having a phenol, a naphthol or an aniline as the coupling component; azomethine dyes having a pyrazolone or a pyrazolotriazole as the coupling component; methine dyes such as arylidene dye, styryl dye, merocyanine dye and oxonol dye; carbonium dyes such as diphenylmethane dye, triphenylmethane dye and xanthene dye; quinone-base dyes such as naphthoquinone, anthraquinone and anthrapyridone; and condensed polycyclic dyes such as dioxazine dye. These dyes may be a dye which provides a magenta color for the first time when a part of the chromophore is dissociated. In this case, the counter cation may be an inorganic cation such as alkali metal and ammonium, an organic cation such as pyridinium and quaternary ammonium salt, or a polymer cation having such a cation as a partial structure.

[0081] Examples of the cyan dye include azomethine dyes such as indoaniline dye and indophenol dye; polymethine dyes such as cyanine dye, oxonol dye and merocyanine dye; carbonium dyes such as diphenylmethane dye, triphenylmethane dye and xanthene dye; phthalocyanine dyes; anthraquinone dyes; aryl- or heteryl-azo dyes having a phenol, a naphthol or an aniline as the coupling component; and indigo-thioindigo dyes. These dyes may be a dye which provides a cyan color for the first time when a part of the chromophore is dissociated. In this case, the counter cation

may be an inorganic cation such as alkali metal and ammonium, an organic cation such as pyridinium and quaternary ammonium salt, or a polymer cation having such a cation as a partial structure.

[0082] A black dye such as polyazo dye can also be used.

[0083] Examples of the water-soluble dye include a direct dye, an acid dye, a food color, a basic dye and a reactive dye. Preferred examples thereof include C.I. Direct Red 2, 4, 9, 23, 26, 31, 39, 62, 63, 72, 75, 76, 79, 80, 81, 83, 84, 89, 92, 95, 111, 173, 184, 207, 211, 212, 214, 218, 21, 223, 224, 225, 226, 227, 232, 233, 240, 241, 242, 243 and 247; C.I. Direct Violet 7, 9, 47, 48, 51, 66, 90, 93, 94, 95, 98, 100 and 101; C.I. Direct Yellow 8, 9, 11, 12, 27, 28, 29, 33, 35, 39, 41, 44, 50, 53, 58, 59, 68, 86, 87, 93, 95, 96, 98, 100, 106, 108, 109, 110, 130, 132, 142, 144, 161 and 163; C.I. Direct Blue 1, 10, 15, 22, 25, 55, 67, 68, 71, 76, 77, 78, 80, 84, 86, 87, 90, 98, 106, 108, 109, 151, 156, 158, 159, 160, 168, 189, 192, 193, 194, 199, 200, 201, 202, 203, 207, 211, 213, 214, 218, 225, 229, 236, 237, 244, 248, 249, 251, 252, 264, 270, 280, 288, 289 and 291; C.I. Direct Black 9, 17, 19, 22, 32, 51, 56, 62, 69, 77, 80, 91, 94, 97, 108, 112, 113, 114, 117, 118, 121, 122, 125, 132, 146, 154, 166, 168, 173 and 199; C.I. Acid Red 35, 42, 52, 57, 62, 80, 82, 111, 114, 118, 119, 127, 128, 131, 143, 151, 154, 158, 249, 254, 257, 261, 263, 266, 289, 299, 301, 305, 336, 337, 361, 396 and 397; C.I. Acid Violet 5, 34, 43, 47, 48, 90, 103 and 126; C.I. Acid Yellow 17, 19, 23, 25, 39, 40, 42, 44, 49, 50, 61, 64, 76, 79, 110, 127, 135, 143, 151, 159, 169, 174, 190, 195, 196, 197, 199, 218, 219, 222 and 227; C.I. Acid Blue 9, 25, 40, 41, 62, 72, 76, 78, 80, 82, 92, 106, 112, 113, 120, 127:1, 129, 138, 143, 175, 181, 205, 207, 220, 221, 230, 232, 247, 258, 260, 264, 271, 277, 278, 279, 280, 288, 290 and 326; C.I. Acid Black 7, 24, 29, 48, 52:1 and 172; C.I. Reactive Red 3, 13, 17, 19, 21, 22, 23, 24, 29, 35, 37, 40, 41, 43, 45, 49 and 55; C.I. Reactive Violet 1, 3, 4, 5, 6, 7, 8, 9, 16, 17, 22, 23, 24, 26, 27, 33 and 34; C.I. Reactive Yellow 2, 3, 13, 14, 15, 17, 18, 23, 24, 25, 26, 27, 29, 35, 37, 41 and 42; C.I. Reactive Blue 2, 3, 5, 8, 10, 13, 14, 15, 17, 18, 19, 21, 25, 26, 27, 28, 29 and 38; C.I. Reactive Black 4, 5, 8, 14, 21, 23, 26, 31, 32 and 34; C.I. Basic Red 12, 13, 14, 15, 18, 22, 23, 24, 25, 27, 29, 35, 36, 38, 39, 45 and 46; C.I. Basic Violet 1, 2, 3, 7, 10, 15, 16, 20, 21, 25, 27, 28, 35, 37, 39, 40 and 48; C.I. Basic Yellow 1, 2, 4, 11, 13, 14, 15, 19, 21, 23, 24, 25, 28, 29, 32, 36, 39 and 40; C.I. Basic Blue 1, 3, 5, 7, 9, 22, 26, 41, 45, 46, 47, 54, 57, 60, 62, 65, 66, 69 and 71; and C.I. Basic Black 8.

[0084] The dye containing the phthalocyanine dye for use in the present invention is substantially soluble or dispersible in water. More specifically, the solubility of the dye in water at 20°C is preferably 10 % by weight or more, more preferably 15 % by weight or more.

[0085] In the ink of the present invention, a pigment can also be used in combination.

[0086] As the pigment for use in the present invention, commercially available pigments and known pigments described in various publications can be used. The publication includes Color Index, compiled by The Society of Dyers and Colourists, Kaitei Shin Han Ganryo Binran (Revised New Handbook of Pigments), compiled by Nippon Gijutsu Kyokai (1989), Saishin Ganryo Oyo Gijutsu (Newest Pigment Application Technology), CMC Shuppan (1986), Insatsu Ink Gijutsu (Printing Ink Technique), CMC Shuppan (1984), and W. Herbst and K. Hunger, Industrial Organic Pigments, VCH Verlagsgesellschaft (1993). Specific examples of the organic pigment include azo pigments (e.g., azo lake pigment, insoluble azo pigment, condensed azo pigment, chelate azo pigment), polycyclic pigments (e.g., phthalocyanine-base pigment, anthraquinone-base pigment, perylene-base and perynone-base pigment, indigo-base pigment, quinacridone-base pigment, dioxazine-base pigment, isoindolinone-base pigment, quinophthalone-base pigment, diketopyrrolopyrrole-base pigment), dyeing lake pigments (lake pigments of acidic or basic dye) and azine pigments. Specific examples of the inorganic pigment include yellow pigments such as C.I. Pigment Yellow 34, 37, 42 and 53, red-base pigments such as C.I. Pigment Red 101 and 108, blue-base pigments such as C.I. Pigment Blue 27, 29 and 17:1, black-base pigments such as C.I. Pigment Black 7 and magnetite, and white-base pigments such as C.I. Pigment White 4, 6, 18 and 21.

[0087] The pigments having a preferred color tone for the formation of an image include the followings. As the blue to cyan pigment, phthalocyanine pigments, anthraquinone-type indanthrone pigments (for example, C.I. Pigment Blue 60) and dyeing lake pigment-type triarylcarbonium pigments are preferred, and phthalocyanine pigments are most preferred (preferred examples thereof include copper phthalocyanine such as C.I. Pigment Blue 15:1, 15:2, 15:3, 15:4 and 15:6, monochloro or low chlorinated copper phthalocyanine, aluminum phthalocyanine such as pigments described in European Patent 860475, nonmetallic phthalocyanine such as C.I. Pigment Blue 16, and phthalocyanine with the center metal being Zn, Ni or Ti, and among these, C.I. Pigment Blue 15:3 and 15:4 and aluminum phthalocyanine are more preferred).

[0088] As the red to violet pigment, azo pigments (preferred examples thereof include C.I. Pigment Red 3, 5, 11, 22, 38, 48:1, 48:2, 48:3, 48:4, 49:1, 52:1, 53:1, 57:1, 63:2, 144, 146 and 184, and among these, C.I. Pigment Red 57:1, 146 and 184 are more preferred), quinacridone-base pigments (preferred examples thereof include C.I. Pigment Red 122, 192, 202, 207 and 209 and C.I. Pigment Violet 19 and 42, and among these, C.I. Pigment Red 122 is more preferred), dyeing lake pigment-type triarylcarbonium pigments (preferred examples thereof include xanthene-base C.I. Pigment Red 81:1 and C.I. Pigment Violet 1, 2, 3, 27 and 39), dioxazine-base pigments (for example, C.I. Pigment Violet 23 and 37), diketopyrrolopyrrole-base pigments (for example, C.I. Pigment Red 254), perylene pigments (for example, C.I. Pigment Violet 29), anthraquinone-base pigments (for example, C.I. Pigment Violet 5:1, 31 and 33) and

thioindigo-base pigments (for example, C.I. Pigment Red 38 and 88) are preferred.

[0089] As the yellow pigment, azo pigments (preferred examples thereof include monoazo pigment-type C.I. Pigment Yellow 1, 3, 74 and 98, disazo pigment-type C.I. Pigment Yellow 12, 13, 14, 16, 17 and 83, synthetic azo-type C.I. Pigment 93, 94, 95, 128 and 155, and benzimidazolone-type C.I. Pigment Yellow 120, 151, 154, 156 and 180, and among these, those not using a benzidine-base compound as a raw material are more preferred), isoindoline-isoindolinone-base pigments (preferred examples thereof include C.I. Pigment Yellow 109, 110, 137 and 139,), quinophthalone pigments (preferred examples thereof include C.I. Pigment Yellow 138) and flavanthrone pigments (for example, C.I. Pigment Yellow 24) are preferred

[0090] As the black pigment, inorganic pigments (preferred examples thereof include carbon black and magnetite) and aniline black are preferred.

[0091] Other than these, an orange pigment (for example, C.I. Pigment Orange 13 and 16) and a green pigment (for example, C.I. Pigment Green 7) may be used.

[0092] The pigment which can be used in the present invention may be the above-described pigment as it is or a pigment after the surface treatment. For the surface treatment, a method of coating the surface with resin or wax, a method of attaching a surfactant, and a method of binding a reactive substance (for example, a radical generated from a silane coupling agent, an epoxy compound, polyisocyanate or a diazonium salt) to the pigment surface may be used and these are described in the following publications and patents:

- (1) Kinzoku Sekken no Seishitsu to Oyo (Properties and Applications of Metal Soap), Saiwai Shobo;
- (2) Insatsu Ink Insatsu (Printing Ink Printing), CMC Shuppan (1984);
- (3) Saishin Ganryo Oyo Gijutsu (Newest Pigment Application Technology), CMC Shuppan (1986);
- (4) U.S. Patents 5,554,739 and 5,571,311; and
- (5) JP-A-9-151342, JP-A-10-140065, JP-A-10-292143 and JP-A-11-166145.

[0093] Particularly, self-dispersible pigments prepared by allowing a diazonium salt to act on carbon black described in U.S. Patents of (4) and encapsulated pigments prepared by the method described in Japanese Patent Publications of (5) are effective because dispersion stability can be obtained without using an excess dispersant in the ink.

[0094] In the present invention, the pigment may be dispersed by further using a dispersant. Various known dispersants can be used according to the pigment used, for example, a surfactant-type low molecular dispersant or a polymer-type dispersant can be used. Examples of the dispersant include those described in JP-A-3-69949 and European Patent 549486. In using the dispersant, a pigment derivative called synergist may also be added so as to accelerate the adsorption of dispersant to the pigment.

[0095] The particle size of the pigment which can be used in the present invention is, after the dispersion, preferably from 0.01 to 10 µm, more preferably from 0.05 to 1 µm.

[0096] As for the method of dispersing the pigment, known dispersion techniques used at the production of ink or toner can be used. Examples of the dispersing machine include vertical or horizontal agitator mill, attritor, colloid mill, ball mill, three-roll mill, bar mill, super-mill, impeller, disperser, KD mill, dynatron and pressure kneader. These are described in detail in Saishin Ganryo Oyo Gijutsu (Newest Pigment Application Technology), CMC Shuppan (1986).

[0097] In a recording medium having an image-receiving layer, the ink of the present invention permeates to a depth of 5 to 30 µm. With the permeation depth in this range, an image having good cyan color and free from generation of bronze can be obtained. The permeation depth is preferably from 8 to 30 µm, more preferably from 10 to 30 µm.

[0098] The permeation depth can be measured, for example, by cutting out a section or a slice of the recording medium using a microtome and observing it through a microscope.

[0099] The permeation depth varies depending on the hydrophilic/hydrophobic balance due to the number of hydrophilic group in the dye, the alkylene chain length in the side chain, the amide bond and the like, but can be controlled by the species of water-miscible organic solvent which is described later, the amount of water-miscible organic solvent or the surfactant. For example, when the dye is hydrophobic, the permeation is generally shallow, however, the permeation can be promoted by additionally adding 2-pyrrolidone, diethylene glycol, triethylene glycol, glycerin, triethanolamine or the like or increasing the amount thereof or by using a surfactant.

[0100] In order to attain a permeation depth in the desired range, the water-miscible organic solvent is preferably used to give a total content of 1 to 60 % by weight, more preferably from 5 to 50 % by weight in the ink. The amount of the surfactant used is preferably from 0.1 to 10 % by weight, more preferably from 0.5 to 6 % by weight.

[0101] The surfactant for use in the present invention is described below.

[0102] Examples of the surfactant for use in the present invention include anionic surfactants such as fatty acid salts, ester salts of higher alcohol, alkylbenzenesulfonates, sulfosuccinic acid ester salts, and phosphoric acid ester salts of higher alcohol; cationic surfactants such as aliphatic amine salts and quaternary ammonium salts; nonionic surfactants such as ethylene oxide adducts of higher alcohol, ethylene oxide adducts of alkylphenol, ethylene oxide adducts of polyhydric alcohol fatty acid ester, acetylene glycol and ethylene oxide adducts thereof; amphoteric surfactants such

as amino acid type and betaine type; and fluorine-containing or silicon-containing compounds. These surfactants can be used individually or in combination of two or more thereof.

[0103] When a surfactant is incorporated into the inkjet recording ink of the present invention and the liquid properties of the ink, such as surface tension, are thereby adjusted, the ejection stability of ink can be improved and an excellent effect can be provided on the elevation of water resistance of image or prevention of blurring of the printed ink.

[0104] The inkjet recording ink of the present invention can be produced by dissolving the above-described phthalocyanine dye in an aqueous medium, adding a specific amount of a surfactant, and if desired, dissolving and/or dispersing other additives. The "aqueous medium" as used in the present invention means water or a mixture of water and a slight amount of water-miscible organic solvent, where additives such as wetting agent, stabilizer and antiseptic are added, if desired.

[0105] At the preparation of the ink solution of the present invention, in the case of a water-soluble ink, the dye is preferably first dissolved in water and thereafter, various solvents and additives are added, dissolved and mixed to provide a uniform ink solution.

[0106] For dissolving the dye and the like, various methods such as stirring, ultrasonic irradiation and shaking can be used. Among these, stirring is preferred. In performing the stirring, various methods known in the art can be used, such as flow stirring and stirring utilizing the shearing force by means of a reversal agitator or a dissolver. Also, a stirring method utilizing the shearing force with the bottom surface of a container, such as magnetic stirrer, can be advantageously used.

[0107] The preparation method of the aqueous ink for ink jetting is described in detail in JP-A-5-148436, JP-A-5-295312, JP-A-7-97541, JP-A-7-82515, JP-A-7-118584 and Japanese Patent Application Nos. 2000-200780 and 2000-249799 and those described in these patent publications can be utilized also in the preparation of the inkjet recording ink of the present invention.

[0108] The aqueous medium may be a mixture mainly comprising water, where a water-miscible organic solvent is added, if desired. Examples of the water-miscible organic solvent include alcohols (e.g., methanol, ethanol, propanol, isopropanol, butanol, isobutanol, sec-butanol, tert-butanol, pentanol, hexanol, cyclohexanol, benzyl alcohol), polyhydric alcohols (e.g., ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, polypropylene glycol, butylene glycol, hexanediol, pentanediol, glycerin, hexanetriol, thiadiglycol), glycol derivatives (e.g., ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monobutyl ether, propylene glycol monomethyl ether, propylene glycol monobutyl ether, dipropylene glycol monomethyl ether, triethylene glycol monomethyl ether, ethylene glycol diacetate, ethylene glycol monomethyl ether acetate, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, ethylene glycol monophenyl ether), amines (e.g., ethanolamine, diethanolamine, triethanolamine, N-methyldiethanolamine, N-ethyldiethanolamine, morpholine, N-ethylmorpholine, ethylenediamine, diethylenetriamine, triethylenetetramine, polyethylenimine, tetramethylpropylenediamine) and other polar solvents (e.g., formamide, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, sulfolane, 2-pyrrolidone, N-methyl-2-pyrrolidone, N-vinyl-2-pyrrolidone, 2-oxazolidone, 1,3-dimethyl-2-imidazolidinone, acetonitrile, acetone). These water-miscible organic solvents can be used in combination of two or more thereof.

[0109] In the case where the above-described phthalocyanine dye is an oil-soluble dye, the ink solution can be prepared by dissolving the oil-soluble dye in a high boiling point organic solvent and emulsification-dispersing it in an aqueous medium.

[0110] The high boiling point organic solvent for use in the present invention preferably has a boiling point of 150°C or more, more preferably 170°C or more.

[0111] Examples of the high boiling point organic solvent include phthalic acid esters (e.g., dibutyl phthalate, dioctyl phthalate, dicyclohexyl phthalate, di-2-ethylhexyl phthalate, decyl phthalate, bis(2,4-di-tert-amylphenyl) isophthalate, bis(1,1-diethylpropyl) phthalate), esters of phosphoric acid or phosphone (e.g., diphenyl phosphate, triphenyl phosphate, tricresyl phosphate, 2-ethylhexyl-diphenyl phosphate, dioctylbutyl phosphate, tricyclohexyl phosphate, tri-2-ethylhexyl phosphate, tridecyl phosphate, di-2-ethylhexylphenyl phosphate), benzoic acid esters (e.g., 2-ethylhexyl benzoate, 2,4-dichlorobenzoate, dodecyl benzoate, 2-ethylhexyl-p-hydroxybenzoate), amides (e.g., N,N-diethyldecanamide, N,N-diethyllaurylamine), alcohols or phenols (e.g., isostearyl alcohol, 2,4-di-tert-amylphenol), aliphatic esters (e.g., dibutoxyethyl succinate, di-2-ethylhexyl succinate, 2-hexyldecyl tetradecanoate, tributyl citrate, diethyl azelate, isostearyl lactate, trioctylcitrate), aniline derivatives (e.g., N,N-dibutyl-2-butoxy-5-tert-octylaniline), chlorinated paraffins (e.g., paraffins having a chlorine content of 10 to 80%), trimesic acid esters (e.g., tributyl trimesate), dodecylbenzene, diisopropylnaphthalene, phenols (e.g., 2,4-di-tert-amylphenyl, 4-dodecyloxyphenol, 4-dodecyloxy carbonylphenol, 4-(4-dodecyloxyphenyl)sulfonyl)phenol), carboxylic acids (e.g., 2-(2,4-di-tert-amylphenoxy)butyric acid, 2-ethoxyoctanedecanoic acid), alkylphosphoric acids (e.g., di-(2-ethylhexyl)phosphoric acid and diphenylphosphoric acid). The high boiling point organic solvent can be used in an amount of, in terms of the mass (weight) ratio to the oil-soluble dye, from 0.01 to 3 times, preferably from 0.01 to 1.0 times.

[0112] These high boiling point organic solvents may be used individually or as a mixture of several kinds [for ex-

ample, tricresyl phosphate and dibutyl phthalate, trioctyl phosphate and di(2-ethylhexyl) sebacate, or dibutyl phthalate and poly(N-tert-butylacrylamide)).

[0113] Examples of the high boiling point organic solvent for use in the present invention, other than the above-described compounds, and the synthesis method of these high boiling organic solvents are described, for example, in U.S. Patents 2,322,027, 2,533,514, 2,772,163, 2,835,579, 3,594,171, 3,676,137, 3,689,271, 3,700,454, 3,748,141, 3,764,336, 3,765,897, 3,912,515, 3,936,303, 4,004,928, 4,080,209, 4,127,413, 4,193,802, 4,207,393, 4,220,711, 4,239,851, 4,278,757, 4,353,979, 4,363,873, 4,430,421, 4,430,422, 4,464,464, 4,483,918, 4,540,657, 4,684,606, 4,728,599, 4,745,049, 4,935,321 and 5,013,639, EP-A-276319, EP-A-286253, EP-A-289820, EP-A-309158, EP-A-309159, EP-A-309160, EP-A-509311, EP-A-510576, East German Patents 147,009, 157,147, 159,573 and 225,240A, British Patent 2091124A, JP-A-48-47335, JP-A-50-26530, JP-A-51-25133, JP-A-51-26036, JP-A-51-27921, JP-A-51-27922, JP-A-51-149028, JP-A-52-46816, JP-A-53-1520, JP-A-53-1521, JP-A-53-15127, JP-A-53-146622, JP-A-54-91325, JP-A-54-106228, JP-A-54-118246, JP-A-55-59464, JP-A-56-64333, JP-A-56-81836, JP-A-59-204041, JP-A-61-84641, JP-A-62-118345, JP-A-62-247364, JP-A-63-167357, JP-A-63-214744, JP-A-63-301941, JP-A-64-9452, JP-A-64-9454, JP-A-64-68745, JP-A-1-101543, JP-A-1-102454, JP-A-2-792, JP-A-2-4239, JP-A-2-43541, JP-A-4-29237, JP-A-4-30165, JP-A-4-232946 and JP-A-4-346338.

[0114] The high boiling point organic solvent is used in a mass (weight) ratio of 0.01 to 3.0 times, preferably from 0.01 to 1.0 times, to the oil-soluble dye.

[0115] In the present invention, the oil-soluble dye or high boiling point organic solvent is used by emulsification-dispersing it in an aqueous medium. At the emulsification-dispersion, a low boiling point organic solvent may be used in combination depending on the case from the viewpoint of emulsifiability. The low boiling point organic solvent which can be used in combination is an organic solvent having a boiling point of about 30°C to 150°C at atmospheric pressure. Preferred examples thereof include esters (e.g., ethyl acetate, butyl acetate, ethyl propionate, β-ethoxyethyl acetate, methylcellosolve acetate), alcohols (e.g., isopropyl alcohol, n-butyl alcohol, secondary butyl alcohol), ketones (e.g., methyl isobutyl ketone, methyl ethyl ketone, cyclohexanone), amides (e.g., dimethylformamide, N-methylpyrrolidone) and ethers (e.g., tetrahydrofuran, dioxane), however, the present invention is not limited thereto.

[0116] In the emulsification dispersion, an oil phase obtained by dissolving the dye in a high boiling organic solvent or depending on the case, in a mixed solvent of a high boiling organic solvent and a low boiling organic solvent is dispersed in an aqueous phase mainly comprising water to form fine oil droplets of the oil phase. At this time, in either one or both of the aqueous phase and the oil phase, additives described later, such as surfactant, wetting agent, dye stabilizer, emulsification stabilizer, antiseptic and fungicide, can be added, if desired.

[0117] In the general emulsification method, an oil phase is added to an aqueous phase, however, a so-called phase inversion emulsification method of adding dropwise an aqueous phase in an oil phase can also be preferably used.

[0118] In performing the emulsification dispersion of the present invention, various surfactants described above can be used. Preferred examples thereof include anionic surfactants such as fatty acid salt, alkylsulfuric ester salt, alkylbenzenesulfonate, alkylnaphthalenesulfonate, dialkylsulfosuccinate, alkylphosphoric ester salt, naphthalenesulfonic acid formalin condensate and polyoxyethylenealkylsulfuric ester salt, and nonionic surfactants such as polyoxyethylene alkylallyl ether, polyoxyethylene fatty acid ester, sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester, polyoxyethylene alkylamine, glycerin fatty acid ester and oxyethylene oxypropylene block copolymer. Also, SURFYNOLS (produced by Air Products & Chemicals), which is an acetylene-base polyoxyethylene oxide surfactant, is preferably used. In addition, amine oxide-type amphoteric surfactants such as N,N-dimethyl-N-alkylamine oxide are preferred. Furthermore, surfactants described in JP-A-59-157636 (pages (37) to (38)) and Research Disclosure, No. 308119 (1989) can be used.

[0119] For the purpose of stabilizing the dispersion immediately after the emulsification, a water-soluble polymer may also be added in combination with the surfactant. As the water-soluble polymer, polyvinyl alcohol, polyvinylpyrrolidone, polyethylene oxide, polyacrylic acid, polyacrylamide, and copolymers thereof are preferably used. In addition, natural water-soluble polymers such as polysaccharides, casein and gelatin are also preferably used. Furthermore, for the stabilization of the dye dispersion, a polymer which does not substantially dissolve in an aqueous medium, such as polyvinyl, polyurethane, polyester, polyamide, polyurea and polycarbonate obtained by the polymerization of acrylic acid esters, methacrylic acid esters, vinyl esters, acrylamides, methacrylamides, olefins, styrenes, vinyl ethers and acrylonitriles, can also be used in combination. This polymer preferably contains -SO<sup>2-</sup> or -COO<sup>-</sup>. In the case of using this polymer which does not substantially dissolve in an aqueous medium, the polymer is preferably used in an amount of 20% by weight or less, more preferably 10% by weight or less, based on the high boiling point organic solvent.

[0120] In preparing an aqueous ink by dispersing an oil-soluble dye or a high boiling point organic solvent according to the emulsification dispersion, control of the particle size is important. In order to elevate the color purity or density of an image formed by the ink jetting, it is essential to reduce the average particle size. The average particle size is, in terms of the volume average particle size, preferably 1 μm or less, more preferably from 5 to 100 nm.

[0121] The volume average particle size and particle size distribution of the dispersed particles can be easily measured by a known method such as static light scattering method, dynamic light scattering method, centrifugal precipitation

- method and the method described in Jikken Kagaku Koza (Lecture of Experimental Chemistry), 4th ed., pp. 417-418. For example, the ink solution is diluted with distilled water such that the particle concentration in the ink becomes from 0.1 to 1 % by weight, then, the particle size can be easily measured by a commercially available volume average particle size measuring apparatus (for example, Microtrac UPA, manufactured by Nikkiso K.K.). The dynamic light scattering method utilizing the laser Doppler effect is particularly preferred because the particle size can be measured even in the case of particles having a small size.
- [0122] The volume average particle size is an average particle size weighted with the particle volume and is obtained by multiplying the diameter of individual particles in the gathering of particles with the volume of the particle and dividing the sum total of the obtained values by the total volume of particles. The volume average particle size is described in 10 Soichi Muroi, Kobunshi Latex no Kagaku (Chemistry of Polymer Latex), page 119, Kobunshi Kankai Kai.
- [0123] Also, it is revealed that the presence of coarse particles greatly affects the printing performance. More specifically, the coarse particle clogs the nozzle of head or even if the nozzle is not clogged, forms a soil to bring about failure or slippage in the ejection of ink and seriously affect the printing performance. In order to prevent these troubles, it is important that when an ink is prepared, the number of particles having a particle size of 5 µm or more and the 15 number of particles having a particle size of 1 µm or more are reduced to 10 or less and 100 or less, respectively, in 1 µl of ink.
- [0124] For removing these coarse particles, a known method such as centrifugal separation or microfiltration can be used. This separation step may be performed immediately after the emulsification dispersion or may be performed 20 immediately before filling the ink in an ink cartridge after various additives such as wetting agent and surfactant are added to the emulsified dispersion.
- [0125] A mechanically emulsifying apparatus is effective for reducing the average particle size and eliminating coarse 25 particles.
- [0126] As the emulsifying apparatus, known apparatuses such as simple stirrer, impeller stirring system, in-line stirring system, mill system such as colloid mill, and ultrasonic system can be used, however, a high-pressure homogenizer is particularly preferred.
- [0127] The mechanism of the high-pressure homogenizer is described in detail in U.S. Patent 4,533,254 and JP-A-6-47264. Examples of the commercially available apparatus include Gaulin Homogenizer (manufactured by A.P. V Gaulin Inc.), Microfluidizer (manufactured by Microfluidex Inc.) and Altimizer (produced by Sugino Machine).
- [0128] The recent high-pressure homogenizer with a mechanism of pulverizing particles in an ultrahigh pressure jet stream described in U.S. Patent 5,720,551 is particularly effective for the emulsification dispersion of the present invention. Examples of the emulsifying apparatus using this ultrahigh pressure jet stream include DeBEE2000 (manufactured by BEE International Ltd.).
- [0129] In performing the emulsification by a high-pressure emulsification dispersing apparatus, the pressure is 50 MPa or more, preferably 60 MPa or more, more preferably 180 MPa or more.
- [0130] A method of using two or more emulsifying apparatuses, for example, emulsification in a stirring emulsifier and then passing through a high-pressure homogenizer, is particularly preferred. Also, a method of once emulsification dispersing the dye solution by such an emulsifying apparatus, adding additives such as wetting agent and surfactant, and then again passing the dispersion through a high-pressure homogenizer until filling the ink into a cartridge is preferred.
- [0131] In the case of containing a low boiling point organic solvent in addition to a high boiling point organic solvent, the low boiling point solvent is preferably removed in view of stability of the emulsified product, safety and hygiene. For removing the low boiling point solvent, various known methods can be used according to the kind of solvent. Examples of the method include evaporation, vacuum evaporation and ultrafiltration. This removal of the low boiling point organic solvent is preferably performed as soon as possible immediately after the emulsification.
- [0132] In the present invention, in the case of using the ink as an inkjet recording ink, additives can be appropriately selected and used in an appropriate amount in addition to those compounds, such as drying inhibitor for preventing clogging due to drying of ink at the ejection port, permeation accelerator for attaining more successful permeation of ink into paper, ultraviolet absorbent, antioxidant, viscosity adjusting agent, surface tension adjusting agent, dispersant, dispersion stabilizer, fungicide, rust inhibitor, pH adjusting agent, defoaming agent and chelating agent.
- [0133] The drying inhibitor for use in the present invention is preferably a water-soluble organic solvent having a vapor pressure lower than water.
- [0134] Specific examples thereof include polyhydric alcohols represented by ethylene glycol, propylene glycol, diethylene glycol, polyethylene glycol, thiadiglycol, dithiodiglycol, 2-methyl-1,3-propanediol, 1,2,6-hexanetriol, acetylene glycol derivative, glycerin and trimethylolpropane; lower alkyl ethers of polyhydric alcohol, such as ethylene glycol monomethyl(or ethyl) ether, diethylene glycol monomethyl(or ethyl) ether and triethylene glycol monoethyl(or butyl) ether; heterocyclic rings such as 2-pyrrolidone, N-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone and N-ethylmorpholine; sulfur-containing compounds such as sulfolane, dimethylsulfoxide and 3-sulfolene; polyfunctional compounds such as diacetone alcohol and diethanolamine; and urea derivatives. Among these, polyhydric alcohols such

as glycerin and diethylene glycol are preferred. These drying inhibitors may be used individually or in combination of two or more thereof. The drying inhibitor is preferably contained in the ink in an amount of 10 to 50 % by weight.

[0135] Examples of the permeation accelerator for use in the present invention include alcohols such as ethanol, isopropanol, butanol, diethylene glycol monobutyl ether, triethylene glycol monobutyl ether and 1,2-hexanediol, sodium laurylsulfate, sodium oleate and nonionic surfactants. A sufficiently high effect can be obtained by adding from 10 to 30 % by weight of the permeation accelerator to the ink. The permeation accelerator is preferably used within the amount range of causing no blurring of printed letter or no print through.

[0136] Examples of the ultraviolet absorbent which can be used for improving the preservability of image in the present invention include benzotriazole-base compounds described in JP-A-58-185677, JP-A-61-190537, JP-A-2-782,

JP-A-5-197075 and JP-A-9-34057, benzophenone-base compounds described in JP-A-46-2784, JP-A-5-194483 and U.S. Patent 3,214,463, cinnamic acid-base compounds described in JP-B-48-30492 (the term "JP-B" as used herein means an "examined Japanese patent publication"), JP-B-56-21141 and JP-A-10-88106, triazine-base compounds described in JP-A-4-298503, JP-A-8-53427, JP-A-8-239368, JP-A-10-182621 and JP-T-8-501291 (the term "JP-T" as used herein means a "published Japanese translation of a PCT patent application"), compounds described in Research Disclosure No. 24239, and compounds of absorbing ultraviolet light and emitting fluorescent light, so-called fluorescent brightening agents represented by stilbene-base compound and benzoxazole-base compound.

[0137] As the antioxidant used for improving the preservability of image in the present Invention, various organic discoloration inhibitors and metal complex-base discoloration inhibitors can be used. Examples of the organic discoloration inhibitor include hydroquinones, alkoxyphenols, dialkoxyphenols, phenols, anilines, amines, indages, chromans, alkoxyanilines and heterocyclic rings. Examples of the metal complex include nickel complex and zinc complex. More specifically, compounds described in patents cited in Research Disclosure, Nos. 17643 (Items VII-I to VII-J), 15162, 18716 (page 650, left column), 36544 (page 527), 307105 (page 872) and 15162, and compounds included in formulæ of representative compounds and in exemplary compounds described in JP-A-62-215272 (pages 127 to 137) can be used.

[0138] Examples of the fungicide for use in the present invention include sodium dehydroacetate, sodium benzoate, sodium pyridinethione-1-oxide, ethyl p-hydroxybenzoate, 1,2-benzisothiazolin-3-one and salts thereof. The fungicide is preferably used in the ink in an amount of 0.02 to 5.00 % by weight. These are described in detail in Bokin Bobai Zai Jiten (Dictionary of Microbicide and Fungicide), compiled by Nippon Bokin Bobai Gakkai Jiten Henshu linkai. Examples of the rust inhibitor include acidic sulfite, sodium thiosulfate, ammon thioglycolate, diisopropylammonium nitrite, pentaerythritol tetranitrate, dicyclohexylammonium nitrite and benzotriazole. The rust inhibitor is preferably used in the ink in an amount of 0.02 to 5.00 by weight.

[0139] The pH adjusting agent for use in the present invention is suitably used for adjusting the pH and imparting dispersion stability. The pH of the ink is adjusted to 8 to 11 at 25°C. If the pH is less than 8, the solubility of dye decreases to readily cause clogging of a nozzle, whereas if it exceeds 11, the water resistance deteriorates. Examples of the pH adjusting agent include, as basic one, organic bases and inorganic alkalis, and as acidic one, organic acids and inorganic acids.

[0140] Examples of the organic base include triethanolamine, diethanolamine, N-methyldiethanolamine and dimethylmethanolamine. Examples of the inorganic alkali include hydroxides of alkali metal, such as sodium hydroxide, lithium hydroxide and potassium hydroxide; carbonates of alkali metal, such as sodium carbonate and sodium hydrogencarbonate; and ammonium. Examples of the organic acid include acetic acid, propionic acid, trifluoroacetic acid and alkylsulfonic acid. Examples of the inorganic acid include hydrochloric acid, sulfuric acid and phosphoric acid.

[0141] The surface tension of the ink for use in the present invention is preferably from 20 to 50 mN/m, more preferably from 20 to 40 mN/m, at 25°C. If the surface tension exceeds 50 mN/m, ejection stability and printing qualities such as blurring and whisker at the color mixing are seriously deteriorated, whereas if the surface tension of ink is less than 20 mN/m, printing failure may occur due to attachment of ink to the hard surface at the ejection.

[0142] The viscosity of the ink for use in the present invention is preferably 30 mPa·s or less, more preferably 20 mPa·s or less. For the purpose of adjusting the viscosity, a viscosity adjusting agent is sometimes used. Examples of the viscosity adjusting agent include celluloses, water-soluble polymers such as polyvinyl alcohol, and nonionic surfactants. These are described in detail in Nendo Chosei Gijutsu (Viscosity Adjusting Technology), Chap. 9, Gijutsu Joho Kyokai (1999), and Inkjet Printer Yo Chemicals (98 Zoho) -Zairyō no Kaihatsu Doko-Tenbo Chosa- (Chemicals for Inkjet Printer (Enlarged Edition of 98) -Survey on Tendency Prospect of Development of Materials-), pp. 162-174, CMC (1997).

[0143] In the present invention, a polymer fine particle dispersion may also be used. This is described in detail in Japanese Patent Application No. 2001-63780.

[0144] In the present invention, if desired, the above-described various cationic, anionic or nonionic surfactants can be used as the dispersant or dispersion stabilizer, and fluorine-base or silicone-base compounds, chelating agents represented by EDTA, and the like can be used as the defoaming agent.

[0145] The ink of the present invention can be used for forming an image on known materials for recording, namely,

plain paper, resin coated paper, inkjet special paper described; for example, in JP-A-8-169172, JP-A-8-27693, JP-A-2-276670, JP-A-7-276789, JP-A-9-323475, JP-A-62-238783, JP-A-10-153989, JP-A-10-217473, JP-A-10-235995, JP-A-10-337947, JP-A-10-217597 and JP-A-10-337947, film, electrophotographic common paper, cloth, glass, metal, ceramic and the like.

5 [0146] The recording paper and recording film used in the inkjet printing using the ink of the present invention are described below. The support which can be used for the recording paper or film is produced, for example, from a chemical pulp such as LBKP and NBKP, a mechanical pulp such as GP, PGW, RMP, TMP, CTMP, CMP and CGP, a waste paper pulp such as DIP, or the like by mixing; if desired, conventionally known additives such as pigment, binder, sizing agent, fixing agent, cation agent and paper strength increasing agent, and then sheeting the mixture using various devices such as Fourdrinier paper machine and cylinder paper machine. Other than these supports, synthetic paper or plastic film may be used. The thickness of the support is preferably from 10 to 250 µm and the basis weight is preferably from 10 to 250 g/m<sup>2</sup>. An ink-accepting layer and a backcoat layer may be provided on the support as it is or may be provided after providing a size press or anchor coat layer using starch, polyvinyl alcohol and the like. The support may also be subjected to a flattening treatment by a calendering device such as machine calender, TG calender and soft calender. In the present invention, the support is preferably paper or plastic film of which both surfaces are laminated with polyolefin (for example, polyethylene, polystyrene, polyethylene terephthalate, polybutene or a copolymer thereof). In the polyolefin, a white pigment (for example, titanium oxide or zinc oxide) or a tinting dye (for example, cobalt blue, ultramarine or neodymium oxide) is preferably added.

20 [0147] The image-accepting layer provided on the support contains a pigment and an aqueous binder. The pigment is preferably a white pigment and examples of the white pigment include inorganic white pigments such as calcium carbonate, kaolin, talc, clay, diatomaceous earth, synthetic amorphous silica, aluminum silicate, magnesium silicate, calcium silicate, aluminum hydroxide, alumina, lithopone, zeolite, barium sulfate, calcium sulfate, titanium dioxide, zinc sulfide and zinc carbonate, and organic pigments such as styrene-base pigment, acryl-base pigment, urea resin and melamine resin. The white pigment contained in the ink-accepting layer is preferably a porous inorganic white pigment and a synthetic amorphous silica and the like having a large pore area are more preferred. The synthetic amorphous silica may be either a silicic acid anhydride obtained by a dry production method (gas phase method) or a silicic acid hydrate obtained by a wet production method. In particular, a silicic acid hydrate is preferred. These pigments may be used in combination of two or more thereof.

30 [0148] Specific examples of the recording paper containing the pigment in the image-receiving layer include those disclosed in JP-A-10-81064, JP-A-10-119423, JP-A-10-157277, JP-A-10-217601, JP-A-11-348409, JP-A-2001-138621, JP-A-2000-43401, JP-A-2000-211235, JP-A-2000-309157, JP-A-2001-96897, JP-A-2001-138627, JP-A-11-91242, JP-A-8-2087, JP-A-8-2090, JP-A-8-2091, JP-A-8-2093, JP-A-8-174992, JP-A-11-192777 and JP-A-2001-301314.

35 [0149] Examples of the aqueous binder contained in the image-accepting layer include water-soluble polymers such as polyvinyl alcohol, silanol-modified polyvinyl alcohol, starch, cationized starch, casein, gelatin, carboxymethyl cellulose, hydroxyethyl cellulose, polyvinylpyrrolidone, polyalkylene oxide and polyalkylene oxide derivatives, and water-dispersible polymers such as styrene butadiene latex and acryl emulsion. These aqueous binders can be used individually or in combination of two or more thereof. Among these, polyvinyl alcohol and silanol-modified polyvinyl alcohol are preferred in the present invention in view of adhesion to the pigment and peeling resistance of the ink-accepting layer.

40 [0150] The image-accepting layer may contain a mordant, a water-proofing agent, a light fastness enhancer, an ozone resistance enhancer, a surfactant and other additives in addition to the pigment and the aqueous binder.

[0151] The mordant added to the image-accepting layer is preferably immobilized and for this purpose, a polymer mordant is preferably used.

45 [0152] The polymer mordant is described in JP-A-48-28325, JP-A-54-74430, JP-A-54-124726, JP-A-55-22766, JP-A-55-142339, JP-A-60-23850, JP-A-60-23851, JP-A-60-23852, JP-A-60-23853, JP-A-60-57836, JP-A-60-60643, JP-A-60-118834, JP-A-60-122940, JP-A-60-122941, JP-A-60-122942, JP-A-60-235134, JP-A-1-161236 and U.S. Patents 2,484,430, 2,548,564, 3,148,061, 3,309,690, 4,115,124, 4,124,386, 4,193,800, 4,273,853, 4,282,305 and 4,450,224. An image-receiving material containing the polymer mordant described in JP-A-1-161236 (pages 212 to 215) is particularly preferred. When the polymer mordant described in this patent publication is used, an image having excellent image quality can be obtained and at the same time, light fastness of the image is improved.

50 [0153] The water-proofing agent is effective for obtaining a water-resistant image. The water-proofing agent is preferably a cationic resin. Examples of the cationic resin include polyamidopolyamine epichlorohydrin, polyethyleneimine, polyaminesulfone, poly-dimethylidiallyl-ammonium chloride and cation polyacrylamide. The content of the cationic resin is preferably from 1 to 15 % by weight, more preferably from 3 to 10 % by weight, based on the entire solid content of the ink-accepting layer.

55 [0154] Examples of the light fastness enhance and the gas resistance enhance include phenol compounds, hindered phenol compounds, thioether compounds, thiourea compounds, thiocyanic acid compounds, amine compounds, hin-

dered amine compounds, TEMPO compounds, hydrazine compounds, hydrazide compounds, amidine compounds, vinyl group-containing compounds, ester compounds, amide compounds, ether compounds, alcohol compounds, sulfonic acid compounds, saccharides, water-soluble reducing compounds, organic acids, inorganic acids, hydroxy group-containing organic acids, benzotriazole compounds, benzophenone compounds, triazine compounds, heterocyclic compounds, water-soluble metal salts, organic metal compounds and metal complexes.

[0155] Specific compound examples thereof include those described in JP-A-10-182621, JP-A-2001-260519, JP-A-2000-260519, JP-B-4-34953, JP-B-4-34513, JP-B-4-34512, JP-A-11-170686, JP-A-60-67190, JP-A-7-276808, JP-A-2000-94829, JP-T-8-512258 and JP-A-11-321090.

[0156] The surfactant functions as a coating aid, a releasability improver, a slipperiness improver or an antistatic agent. The surfactant is described in JP-A-62-173463 and JP-A-62-183457.

[0157] In place of the surfactant, an organic fluoro compound may be used. The organic fluoro compound is preferably hydrophobic. Examples of the organic fluoro compound include a fluorine-containing surfactant, an oily fluorine-base compound (for example, fluorine oil) and a solid fluorine compound resin (for example, ethylene tetrafluoride resin). The organic fluoro compound is described in JP-B-57-9053 (columns 8 to 17), JP-A-61-20994 and JP-A-62-135826.

[0158] As the hardening agent, for example, the materials described in JP-A-1-161236 (page 222), JP-A-9-263036, JP-A-10-119423 and JP-A-310547 can be used.

[0159] Other additives added to the ink-accepting layer include a pigment dispersant, a thickener; a defoaming agent, a dye, a fluorescent brightening agent, an antiseptic, a pH adjusting agent, a matting agent, a hardening agent and the like. The ink-accepting layer may be composed of either one layer or two layers.

[0160] In the recording paper or film, a backcoat layer may also be provided. Examples of the component which can be added to this layer include a white pigment, an aqueous binder and other components. Examples of the white pigment contained in the backcoat layer include white inorganic pigments such as precipitated calcium carbonate, heavy calcium carbonate, kaolin, talc, calcium sulfate, barium sulfate, titanium dioxide, zinc oxide, zinc sulfide, zinc carbonate, satin white, aluminum silicate, diatomaceous earth, calcium silicate, magnesium silicate, synthetic amorphous silica, colloidal silica, colloidal alumina, pseudo-boehmite, aluminum hydroxide, alumina, lithopone, zeolite, hydrolyzed halloysite, magnesium carbonate and magnesium hydroxide, and organic pigments such as styrene-base plastic pigment, acryl-base plastic pigment, polyethylene, microcapsule, urea resin and melamine resin.

[0161] Examples of the aqueous binder contained in the backcoat layer include water-soluble polymers such as styrene/maleate copolymer, styrene/acrylate copolymer, polyvinyl alcohol, silanol-modified polyvinyl alcohol, starch, cationized starch, casein, gelatin, carboxymethyl cellulose, hydroxyethyl cellulose and polyvinylpyrrolidone, and water-dispersible polymers such as styrene butadiene latex and acryl emulsion. Other components contained in the backcoat layer include a defoaming agent, a foam inhibitor, a dye, a fluorescent brightening agent, an antiseptic, a water-proofing agent and the like.

[0162] A polymer latex may be added to a constituent layer (including the back layer) of the inkjet recording paper or film. The polymer latex is used for the purpose of improving film properties, for example, stabilizing dimension and preventing curling, adhesion or film cracking. The polymer latex is described in JP-A-62-245258, JP-A-62-1316648 and JP-A-62-110066. When a polymer latex having a low glass transition temperature (40°C or less) is added to a layer containing the mordant, the layer can be prevented from cracking or curling. Also, by adding a polymer latex having a high glass transition temperature to the back layer, curling can be prevented.

[0163] The ink of the present invention is not limited on the inkjet recording system and is used in a known system, for example, an electric charge controlling system of jetting out the ink by using the electrostatic induction force, a drop-on-demand system (pressure pulse system) using an oscillation pressure of a piezoelectric device, an acoustic inkjet system of converting electric signals into acoustic beams, irradiating the beams on the ink and jetting out the ink using the radiation pressure, or a thermal inkjet system of heating the ink to form bubbles and utilizing the generated pressure.

[0164] The inkjet recording system includes a system of ejecting a large number of small volumes of so-called photo-ink having a low concentration, a system designed to improve the image quality by using a plurality of inks substantially the same in hue but different in the concentration, and a system using colorless transparent ink.

[0165] The inkjet recording ink of the present invention can be used for uses other than the inkjet recording, such as a material for display image, an image-forming material for interior decoration and an image-forming material for outdoor decoration.

[0166] Examples of the material for display image include various materials such as poster, wall paper, ornamental goods (e.g., ornament, doll), handbill for commercial advertisement, wrapping paper, wrapping material, paper bag, vinyl bag, package material, billboard, image drawn or attached to the side face of traffic (e.g., automobile, bus, electric car), and clothes with a logo. In the case of using the dye of the present invention as a material for forming a display image, the image includes, in addition to a strict image, all patterns by a dye, which can be acknowledged by a human, such as abstract design, letter and geometrical pattern.

[0167] Examples of the material for interior decoration include various materials such as wall paper, ornamental

goods (e.g., ornament, doll), member of luminaire, member of furniture and design member of floor or ceiling. In the case of using the dye of the present invention as a material for forming an image, the image includes, in addition to a strict image, all patterns by a dye, which can be acknowledged by a human, such as abstract design, letter and geometrical pattern.

- 5 [0168] Examples of the material for outdoor decoration include various materials such as wall material, roofing material, billboard, gardening material, outdoor ornamental goods (e.g., ornament, doll), and member of outdoor luminaire. In the case of using the dye of the present invention as a material for forming an image, the image includes, in addition to a strict image, all patterns by a dye, which can be acknowledged by a human, such as abstract design, letter and geometrical pattern.
- 10 [0169] In these uses, examples of the medium where the pattern is formed include various materials such as paper, fiber, cloth (including non-woven fabric), plastic, metal and ceramic. Examples of the dyeing form include mordanting, printing and fixing of a dye in the form of a reactive dyestuff having introduced thereto a reactive group. Among these, preferred is dyeing by mordanting.

15 EXAMPLES

[0170] The present invention is described below by referring to Examples, however, the present invention is not limited thereto.

20 (Example 1)

[0171] Deionized water was added to the following components to make 1 liter and the resulting solution was stirred for 1 hour under heating at 30 to 40°C. Thereafter, the solution was filtered under reduced pressure through a microfilter having an average pore size of 0.25 µm to prepare an ink solution for cyan color.

25

Cyan dye of the Present Invention (Compound 154)	17.5 g/liter
Diethylene glycol	167 g/liter
Glycerin	164 g/liter
Triethylene glycol monobutyl ether	125 g/liter
Triethanolamine	6.5 g/liter
Benzotriazole	0.07 g/liter
PROXEL XL2	3.5 g/liter
Surfactant (w-1)	10 g/liter

35

[0172] A magenta ink, a light magenta ink, a cyan ink, a yellow ink a dark yellow ink and a black ink were prepared by using a magenta dye, a yellow dye or a black dye as the dye species in place of the cyan dye and changing the additives, and thereby Ink Set 101 shown in Table 12 was prepared.

40

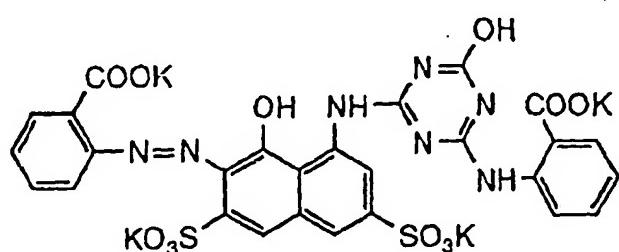
[Table 12]

	Light Cyan	Cyan	Light Magenta	Magenta	Yellow	Dark Yellow	Black
Dye (g/liter)	154 17.5	154 68.0	A-1 10.2	A-1 30.8	A-3 14.0 A-4 14.0	A-3 10.0 A-4 10.0 A-2 13.0	A-5 20.0 A-6 39.0 A-7 17.0 A-3 20.0
Diethylene glycol (g/liter)	167	110	47	76	85	-	20
Urea (g/liter)	-	-	37	46	-	-	-
Glycerin (g/liter)	164	148	198	150	154	147	120
Triethylene glycol monobutyl ether (g/liter)	125	132	105	107	130	127	-

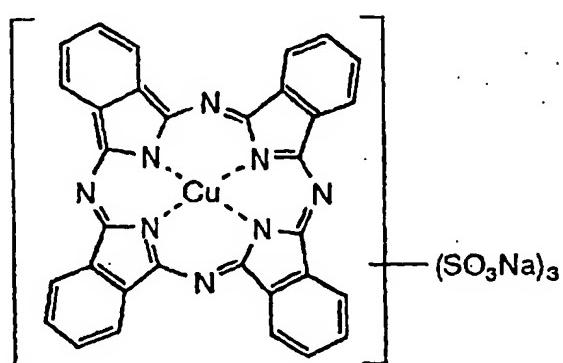
[Table 12] (continued)

	Light Cyan	Cyan	Light Magenta	Magenta	Yellow	Dark Yellow	Black
5	Diethylene glycol monobutyl ether (g/liter)	-	-	-	-	-	230
10	2-Pyrrolidone (g/liter)	-	20	40	-	-	80
15	Surfactant (g/liter)	10	10	6	12	3	5
20	Triethanolamine (g/liter)	6.5	10	7	7	1	18
25	Benzotriazole (g/liter)	0.07	0.09	0.07	0.08	0.06	0.08
30	Proxel XL2 (g/liter)	3.5	4.0	5.0	4.5	3	4
35	Deionized water was added to make 1 liter.						

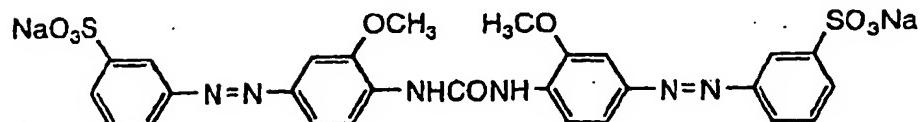
A-1



A-2

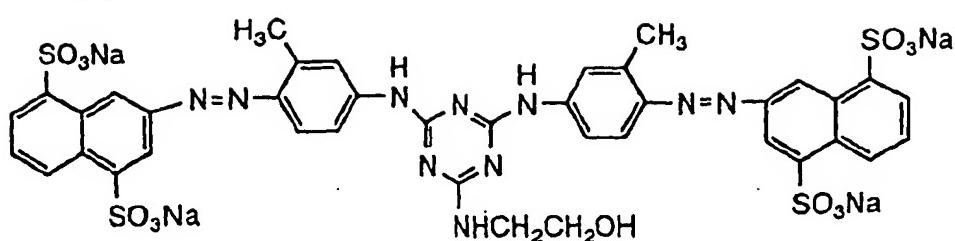


A-3



5

A-4

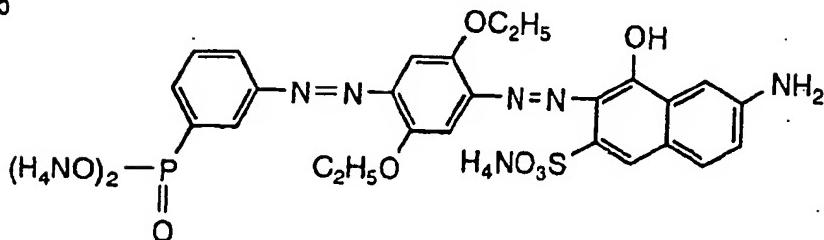


10

15

20

A-5

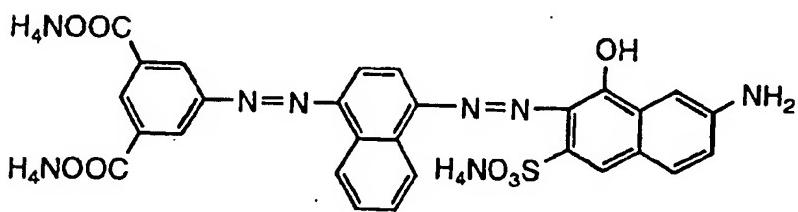


25

30

35

A-6

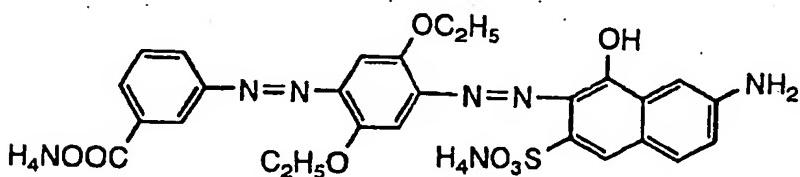


40

45

50

A-7

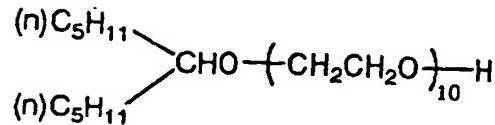


55

5

(W-1)

10



15

[0173] Ink Sets 102 to 108 were prepared in the same manner as Ink Set 101 except that the dye species, surfactant species and amount added of the light cyan ink and the cyan ink of Ink Set 101 were changed as shown in Table 13 below. The permeation depth was measured by preparing a solid image printed sample of cyan, cutting out the section thereof using a microtome (Model MT2-B, manufactured by SORVALL) and observing it through a microscope.

20

25

Ink Set	Light Cyan	Cyan	Permeation Depth, μm	Remarks
101	154	154	20	Invention
102	108	108	23	Invention
103	109	109	23	Invention
104	110	110	10	Invention
105	110	110	3	Comparison
106	149	149	3	Comparison
107	EPSON genuine ink (PM-920C)	EPSON genuine ink (PM-920C)	12	Comparison
108	A-1	A-1	11	Comparison

30

35

(Inkjet Recording)

[0174] Ink Sets 101 to 108 prepared above each was filled in a cartridge of an inkjet printer PM920C (manufactured by Seiko Epson Corporation) and an image was printed-on inkjet paper Photo-Gloss Paper EX produced by Fuji Photo Film Co., Ltd. using the printer. The following evaluations were performed and the results obtained are shown in Table 13.

(1) As the printing performance (i), the cartridge was set in the printer and after confirming the ejection of ink from all nozzles, 20 sheets of A4 paper were output and evaluated on the disorder of printing.

45

A: No disorder of printing from the start to the end of printing.

B: Disorder of printing was generated.

C: Printing was disordered from the start to the end of printing.

50

As the printing performance (ii), the cartridge was left standing at 60°C for 2 days and the disorder of printing was evaluated by the same method as the printing performance (i).

55

(2) As for the image preservability, a solid image printed sample of cyan was prepared to have a reflection density of 1 and evaluated on the following matters.

(i) Light Fastness

[0175] The image density Ci immediately after printing was measured by X-Rite 310 and thereafter, xenon light

(85,000 lx) was irradiated on the image for 6 days using a weather meter manufactured by Atlas. The image density Cf was again measured and the dye residual percentage Ci/Cf\*100 was determined and evaluated. The dye residual percentage was evaluated at three points having a reflection density was 1, 1.5 and 2. The light fastness was rated A when the dye residual percentage was 80% or more at any density, rated B when less than 80% at two points, and rated C when less than 80% at all densities.

5 (ii) Heat Fastness

[0176] The sample was stored for 5 days under the conditions of 80 to 70% RH and the density before and after the storage was measured by X-Rite 310. The dye residual percentage was determined and evaluated. The dye residual percentage was evaluated at three points having a reflection density of 1, 1.5 and 2. The heat fastness was rated A when the dye residual percentage was 90% or more at any density, rated B when less than 90% at two points, and rated C when less than 90% at all densities.

10 (iii) Ozone Resistance

[0177] The sample was stored for 7 days under the conditions heated at 80°C while passing outside air and the image density before and after the storage was measured by a reflection densitometer (X-Rite 310TR). The dye residual percentage was determined and evaluated. The dye residual percentage was evaluated at three points having a reflection density of 1, 1.5 and 2. The ozone resistance was rated A when the dye residual percentage was 90% or more at any density, rated B when less than 90% at two points, and rated C when less than 90% at all densities.

15 (3) The image quality was evaluated as follows by observing the presence or absence of generation of bronze phenomenon with an eye.

- 20  
25 O: No generation of bronze phenomenon.  
x: Bronze phenomenon was generated.

30

35

40

45

50

55

[Table 14]

Ink Set	Printing Performance (i)	Printing Performance (ii)	Light Fastness	Heat Fastness	Ozone Resistance	Image Quality	Remarks
101	A	A	A	A	A	O	Invention
102	A	A	A	A	A	O	Invention
103	A	A	A	A	A	O	Invention
104	A	A	A	A	A	O	Invention
105	A	A	A	A	A	X	Comparison
106	A	A	A	A	A	X	Comparison
107	A	A	B	B	C	O	Comparison
108	A	A	B	B	C	O	Comparison

[0178] It is seen that when the ink composition of the present invention is used for the inkjet recording, excellent printing performance is obtained and the fastness and ozone resistance are also excellent. Furthermore, with the ink of the present invention, an excellent image quality free of bronze phenomenon is revealed.

[0179] The same effect as above are obtained even when the image-receiving paper used in the present invention is changed to PM photographic paper produced by Seiko Epson Corporation or PR101 produced by Canon Inc.

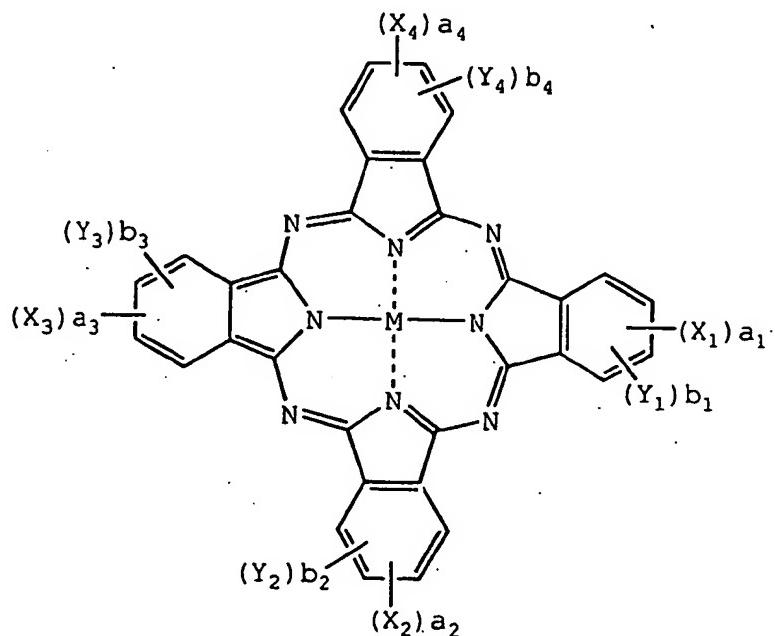
[0180] According to the present invention, an inkjet recording ink having high ejection stability, good color and excellent weather resistance and capable of giving a recorded image having excellent image quality can be provided.

[0181] This application is based on Japanese Patent application JP 2002-101347, filed April 3, 2002, the entire content of which is hereby incorporated by reference, the same as if set forth at length.

10

## Claims

- 15 1. An ink comprising an aqueous medium and at least one dye represented by the following formula (I) which is dissolved or dispersed in the aqueous medium, wherein the ink permeates into a recording medium having an image-receiving layer to a depth of 5 to 30  $\mu\text{m}$ :

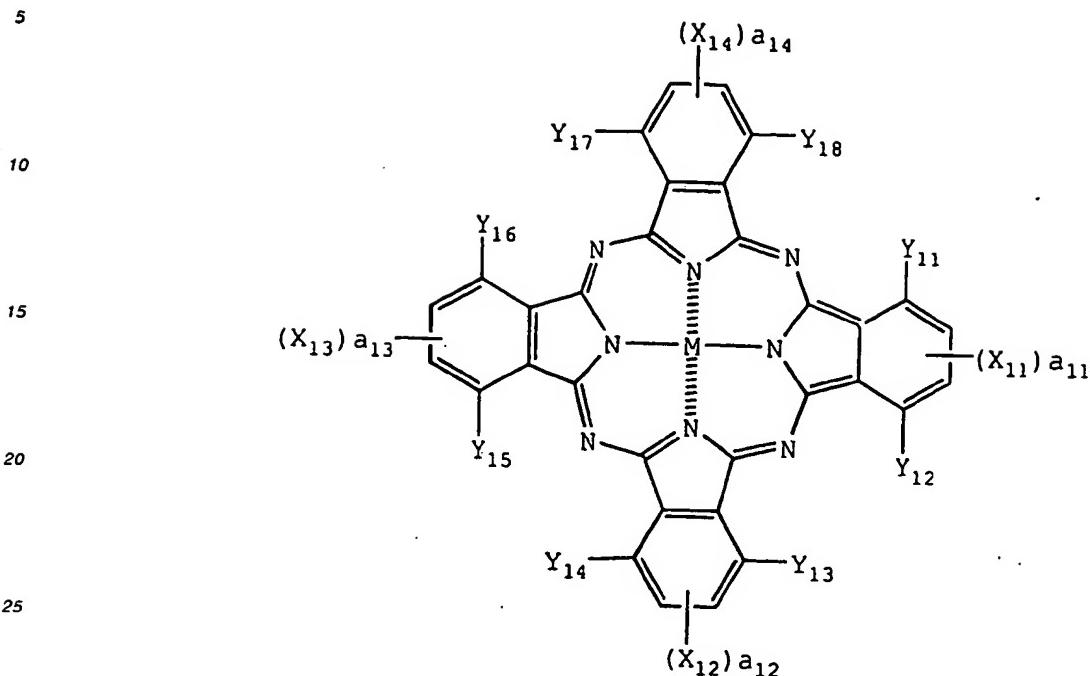


40

wherein X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub> and X<sub>4</sub> each independently represents -SO-Z, -SO<sub>2</sub>-Z, -SO<sub>2</sub>NR<sub>1</sub>R<sub>2</sub>, a sulfo group, -CONR<sub>1</sub>R<sub>2</sub> or -CO<sub>2</sub>R<sub>1</sub>, each Z independently represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic group, R<sub>1</sub> and R<sub>2</sub> each independently represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic group, Y<sub>1</sub>, Y<sub>2</sub>, Y<sub>3</sub> and Y<sub>4</sub> each independently represents a monovalent substituent, a<sub>1</sub> to a<sub>4</sub> and b<sub>1</sub> to b<sub>4</sub> each represents a number of substituent X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub>, X<sub>4</sub>, Y<sub>1</sub>, Y<sub>2</sub>, Y<sub>3</sub> or Y<sub>4</sub>, a<sub>1</sub> to a<sub>4</sub> each independently represents a number of 0 to 4, provided that at least one of a<sub>1</sub> to a<sub>4</sub> does not represent 0, b<sub>1</sub> to b<sub>4</sub> each independently represents a number of 0 to 4, provided that when at least one of a<sub>1</sub> to a<sub>4</sub> and b<sub>1</sub> to b<sub>4</sub> each represents a number of 2 or more, corresponding plurality of substituents X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub>, X<sub>4</sub>, Y<sub>1</sub>, Y<sub>2</sub>, Y<sub>3</sub> or Y<sub>4</sub> may be the same or different, and M represents a hydrogen atom, a metal atom or an oxide, hydroxide or halide thereof.

55

2. The ink according to claim 1, wherein the dye represented by the formula (I) is a dye represented by the following formula (II) :



wherein  $X_{11}$ ,  $X_{12}$ ,  $X_{13}$  and  $X_{14}$  each independently represents -SO-Z, -SO<sub>2</sub>-Z, -SO<sub>2</sub>NR<sub>1</sub>R<sub>2</sub>, a sulfo group, -CONR<sub>1</sub>R<sub>2</sub> or -CO<sub>2</sub>R<sub>1</sub>, Y<sub>11</sub> to Y<sub>18</sub> each independently represents a monovalent substituent, M represents a hydrogen atom, a metal atom or an oxide, hydroxide or halide thereof, and a<sub>11</sub> to a<sub>14</sub> each independently represents an integer of 1 or 2, provided that when at least one of a<sub>11</sub> to a<sub>14</sub> each represents a number of 2, corresponding plurality of substituents X<sub>11</sub>, X<sub>12</sub>, X<sub>13</sub> or X<sub>14</sub> may be the same or different.

- 35 3. The ink according to claim 1, wherein an amount of the dye represented by the formula (I) is from 0.2 to 20 % by weight.
- 40 4. The ink according to claim 2, wherein an amount of the dye represented by the formula (II) is from 0.2 to 20 % by weight.
- 45 5. An inkjet recording method comprising ejecting of the ink according to claim 1.
6. An inkjet recording method comprising ejecting of the ink according to claim 2.
- 50 7. An inkjet recording method comprising:  
preparing an image-receiving material which comprises a support and an image-receiving layer comprising white inorganic pigment particles; and  
ejecting an ink droplet comprising the ink according to claim 1 to the image-receiving material according to recording signals so as to record an image on the image-receiving material.
8. An inkjet recording method comprising:  
preparing an image-receiving material which comprises a support and an image-receiving layer comprising white inorganic pigment particles; and  
ejecting an ink droplet comprising the ink according to claim 2 to the image-receiving material according to recording signals so as to record an image on the image-receiving material.



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number

EP 03 00 7384

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 5 882 390 A (KOJIMA AKIO ET AL) 16 March 1999 (1999-03-16) * column 3, line 6 - column 13, line 35; claims; examples *	1-8	C09D11/00 C09B47/04 C09B47/06 C09B47/067
P,X	EP 1 270 677 A (HEWLETT PACKARD CO) 2 January 2003 (2003-01-02) * page 4 - page 14; claims; examples *	1-8	
X	US 6 123 761 A (HEALY THOMAS) 26 September 2000 (2000-09-26) * column 3, line 30 - column 4, line 60; claims; examples *	1-8	
X	US 6 241 789 B1 (AESCHILMANN PETER ET AL) 5 June 2001 (2001-06-05) * column 2, line 1 - line 20 * * column 6, line 8 - line 36 *	1-8	
X	WO 01 66648 A (PATEL PRAKASH ;AVECIA LTD (GB); WIGHT PAUL (GB)) 13 September 2001 (2001-09-13) * examples *	1-8	
X	GB 1 356 837 A (ICI LTD) 19 June 1974 (1974-06-19) * page 1, line 51 - line 60 *	1-8	C09D C09B
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
MUNICH	5 June 2003	Schmitz, V	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 03 00 7384

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

05-06-2003

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 5882390	A	16-03-1999	JP	10036741 A	10-02-1998
EP 1270677	A	02-01-2003	US	2003041775 A1	06-03-2003
			EP	1270677 A2	02-01-2003
US 6123761	A	26-09-2000	AT	225384 T	15-10-2002
			AU	5515499 A	21-03-2000
			BR	9913228 A	17-07-2001
			CA	2336525 A1	09-03-2000
			CN	1315987 T	03-10-2001
			DE	69903327 D1	07-11-2002
			DK	1108001 T3	10-02-2003
			WO	0012633 A1	09-03-2000
			EP	1108001 A1	20-06-2001
			ES	2182560 T3	01-03-2003
			JP	2002523605 T	30-07-2002
			US	6284031 B1	04-09-2001
US 6241789	B1	05-06-2001	US	2001013149 A1	16-08-2001
			BR	9805323 A	14-12-1999
			EP	0922735 A1	16-06-1999
			JP	11263922 A	28-09-1999
			TW	446734 B	21-07-2001
			US	6063137 A	16-05-2000
WO 0166648	A	13-09-2001	AU	3208001 A	17-09-2001
			WO	0166648 A1	13-09-2001
GB 1356837	A	19-06-1974	AU	4815972 A	02-05-1974
			BE	791163 A1	09-05-1973
			DE	2256544 A1	24-05-1973
			FR	2160556 A1	29-06-1973
			IT	970025 B	10-04-1974
			JP	48075627 A	12-10-1973
			NL	7215018 A	21-05-1973